AD-A260 358

DEACTIVATION OF OXIDATION CATALYSTS

S. K. AGARWAT, J. J. SPIVEY

RESEARCH TRIANGLE INSTITUTE
P. O. BOX 12194
RESEARCH TRIANGLE PARK NC 27709
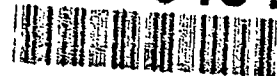
DTIC
S ELECTE D
JAN 2 6 1993
C

MAY 1991

FINAL REPORT

MAY 1989 - MAY 1991

93-01342

AFSSC

AIR FORCE ENGINEERING & SERVICES CENTER
ENGINEERING & SERVICES LABORATORY
TYNDALL AIR FORCE BASE, FLORIDA 32403

REPORT DOCUMENTATION PAGE		Form Approved OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION Unclassified	1b. RESTRICTIVE MARKINGS N/A

2a. SECURITY CLASSIFICATION AUTHORITY N/A	3. DISTRIBUTION / AVAILABILITY OF REPORT
2b. DECLASSIFICATION / DOWNGRADING SCHEDULE N/A	Approved for public release Distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S) ESL TR-91-23

6a. NAME OF PERFORMING ORGANIZATION Research Triangle Institute	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION HQ AFESC/RDVW

6c. ADDRESS (City, State, and ZIP Code) P. O. Box 12194 Research Triangle Park, NC 27709	7b. ADDRESS (City, State, and ZIP Code) Tyndall AFB, FL 32403

8a. NAME OF FUNDING / SPONSORING ORGANIZATION HQ AFESC/RDVW	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER F08635-89-C-0276

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO	PROJECT NO.	TASK NO	WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification)

Deactivation of Oxidation Catalysts

12. PERSONAL AUTHOR(S)
S. K. Agarwal and J. J. Spivey

13a. TYPE OF REPORT Final	13b. TIME COVERED FROM May, 89 TO May, 91	14. DATE OF REPORT (Year, Month, Day) May, 91	15. PAGE COUNT 130

16. SUPPLEMENTARY NOTATION

Availability of this report is specified on reverse of front cover.

17.	COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Catalyst, deactivation, oxidation, volatile organics, noble metal, metal oxide

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Activity and selectivity data for the oxidation of VOC containing air streams are reported over four commercial oxidation catalysts. The effect of VOC type and concentrations was investigated by using three different air streams containing VOCs typical of those expected from Air Force Groundwater air-strippers. The effect of reactor type was investigated by using the ARI catalyst both in the fixed bed and in the fluid bed reactor. The oxidation reaction was conducted for extended periods of time at constant total conversion (>99%). The temperature was periodically increased to compensate for any loss in the intrinsic catalyst activity because of deactivation. The fresh and used catalysts were characterized to correlate the activity and selectivity with the physico-chemical properties of the catalyst.

(Continued)

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL Capt. Edward G. Marchand	22b. TELEPHONE (Include Area Code) (904) 283-6023	22c. OFFICE SYMBOL HQAFESCRDVW

DD Form 1473, JUN 86	Previous editions are obsolete	SECURITY CLASSIFICATION OF THIS PAGE

19. Abstract. (Continued)

A 0.1% Pt/3% Ni/Al$_2$O$_3$ catalyst (G-43A, United Catalysts, Inc., Louisville, Ky) did not lose any activity at 430°C when used continuously for 253 days-on-stream for the oxidation of hydrocarbon stream. On the other hand, a ceria-promoted hopcalite catalyst suffered considerable deactivation and required a temperature increase of 85°C over 297 days-on-stream to maintain the total conversion above 99%. However, the final temperature (400°C) required to maintain >99% conversion over the hopcalite catalyst was still lower than the initial temperature required for the operation of the Pt/Ni catalyst (430°C). No partial oxidation products were formed over either of the catalysts. Also, the only deep oxidation product was CO$_2$.

The catalytic activity and selectivity were found to be a function of the type of feed stream and the reactor configuration. Although the chromia alumina catalyst (EconAbator, ARI Technologies, Inc., Palatine, IL) used for the oxidation of the chlorinated stream did not require any temperature increase when used for 153 days-on-stream in a fixed bed reactor, the results suggest progressive loss in catalyst activity down the catalyst bed. A fluid bed reactor was found to be more effective than a fixed bed reactor in maintaining the catalyst activity for the oxidation of the chlorinated stream. The physical attrition of catalyst particles in the fluid bed reactor accompanied with the loss of chromium, via oxychloride formation, appears to be beneficial in maintaining the catalyst activity by constantly exposing the fresh catalyst surface. The chromia alumina catalyst used for mixed stream oxidation required a temperature increase of 33°C over 210 days-on-stream to maintain constant conversion. This decrease in catalytic activity was related to a decrease in BET surface area.

A simple deactivation model was developed for the Carus catalyst used for the oxidation of hydrocarbon stream. This model can be used to predict the catalyst life-time. A detailed economic analysis was conducted to compare the cost of operation of different catalysts.

EXECUTIVE SUMMARY

A. OBJECTIVE

The main objective of this work was to study the deactivation of commercial catalysts used to oxidize volatile organic compounds (VOCs) from gas streams typical of those produced by air-stripping operations. A standard test procedure is provided in this report for evaluating catalysts for VOC oxidation.

B. BACKGROUND

The installation restoration program (IRP) under way at numerous Air Force bases has identified several sites with contaminated soil and groundwater. This subsurface contamination is the result of fuels, cleaning solvents, and degreasers entering the subsurface environment from accidental spills, leaking storage tanks, and past disposal practices. HQ AFESC/RDVW is conducting research aimed at developing treatment strategies for groundwater cleanup and studying the fate and transport of contaminants in subsurface systems. Many of the contaminants of concern are volatile compounds. These volatile contaminants can be transferred to an air stream by using air strippers. The contaminated air can be passed over a catalyst to oxidize the contaminants to innocuous substances such as CO_2 and H_2O. The catalyst used for the oxidation of VOCs ages with time, i.e., the activity and/or selectivity changes with time. For many applications, it is important to maintain a constant activity to meet environmental regulations. This requires increasing the operating temperature for a deactivating catalyst. Also, the selectivity is important because the partially oxidized product may be more toxic than the original compound. It is therefore necessary to understand the mechanisms of deactivation to devise ways to increase the catalyst life.

C. SCOPE

This report presents the experimental data of hydrocarbon conversion as a function of time on stream for four commerical oxidation catalysts. A short review on catalyst deactivation is presented in Section II along with a detailed literature review on catalyst deactivation in Appendix D. A first-order deactivation model has been developed for the Carulite catalyst. Detailed economic analysis comparing the cost of operation of the four catalysts is also presented. Finally, a standard test protocol has been included for evaluating oxidation catalysts.

D. METHODOLOGY

The catalyst deactivation is a function of the type and concentration of the organics in the gas. Most of the Air Force sites contain a mixture of both hydrocarbon and chlorocarbon compounds. As a result, catalyst deactivation was investigated using three different feed streams containing hydrocarbons, chlorocarbons, and a mixture of both

hydrocarbons and chlorocarbons. Four different commercial catalysts were tested for an extended period of time to oxidize air streams containing VOCs typical of those expected from Air Force groundwater air strippers. The purpose of this was to provide the Air Force with a deactivation mechanism directly pertinent to the control of air stripping emissions at specific Air Force Bases.

E. TEST DESCRIPTION

The catalyst deactivation was studied in four fixed-bed and two fluid-bed laboratoiy scale reactors. These reactors were operated continuously at atmospheric pressure. The three feed streams were generated by blending equal volumes of premixed VOC-containing air with VOC-free air saturated with water vapor. The effluent gases were analyzed by an on-line gas chromotagraph (GC) equipped with a flame ionization detector and a thermal conductivity detector. The GC was used to analyze the VOCs, CO, and CO_2. The chlorine and hydrogen chloride analysis was conducted using Dräger tubes.

F. RESULTS

The oxidation reaction was conducted at constant conversion (above 99 percent) for continuous periods of time (24 hours/day, 7 days/week). The temperature was periodically increased to compensate for any loss in the catalyst activity because of deactivation. Of the two catalysts tested for hydrocarbon conversion, the G-43A catalyst $(Pt,Ni/Al_2O_3)$ did not show any deactivation for 249 days on stream. The other catalyst, Carus (cerium promoted hopcalite), suffered significant deactivation. The temperature had to be increased by 85 °C over 297 days on stream to maintain the total carbon conversion above 99 percent. There were no partial oxidation products formed over either of the catalysts.

Two catalysts, ARI and the Dedert Topsoe's CK-302, were used for the oxidation of both chlorinated and mixed streams. The CK-302 catalyst did not exhibit any deactivation for either stream when used for 247 days for the chlorinated stream and 129 days for the mixed stream oxidation.

The ARI catalyst is designed for fluid-bed operation but was tested both in the fixed- and fluid-bed reactors to investigate the effect of reactor type. The ARI catalyst used for the oxidation of chlorinated stream in the fixed-bed reactor did not show any change in the overall activity for 153 days on stream. However, the CO/CO_2 ratio, a measure of the oxidation power of the catalyst, increased from 0.47 to 1.17 in 153 days. Furthermore, the used catalyst revealed a distinct color change from brown to green in the upstream third of the bed. The next third of the bed was greenish brown while the remaining third of the bed had the original brown color. These results suggest the propagation of a deactivation wave through the catalyst bed.

The ARI catalyst used for the oxidation of the chlorinated stream in the fluid-bed reactor did not exhibit any significant deactivation. However, the ARI catalyst used for mixed-stream oxidation in the fluid-bed reactor did deactivate and the temperature had to be increased by 33 °C over 210 days on stream to maintain a constant conversion. These two used catalysts were characterized by BET, elemental analysis, and X-ray photoelectron spectroscopy (XPS). The surface area of the catalyst used for mixed-stream oxidation decreased by 20 percent suggesting that some catalyst sintering occurred during reaction. The chromium content of this catalyst did not change during the reaction. The ARI catalyst used for chlorinated stream oxidation did not show any change either in the BET surface area or in the Cr 2p binding energy. However, the chromium content decreased by 10 percent probably because of the formation of volatile chromium oxychloride.

A simple mathematical model was developed to fit the deactivation data over the Carus catalyst, which was the only catalyst to show deactivation significant enough to model the process. The model predicted a total catalyst lifetime of 362 days, assuming the maximum operating temperature for this catalyst is 500 °C.

An economic analysis was conducted to rank the best catalyst for the oxidation of hydrocarbons, chlorocarbons, and mixed stream. For the periods of time over which results can be compared, the results show that the ARI and CK-302 costs are essentially equal for the chlorinated stream and that the CK-302 is more cost-effective for the mixed stream. For the hydrocarbon stream, the Carus catalyst, even though it deactivates, is more cost-effective than the G-43A because it operates at a lower temperature.

G. CONCLUSIONS

Based on the results obtained in this work, the catalysts can be ranked for optimum performance and economics as shown in Table E-1.

It should be noted that none of the catalysts completely deactivated in the timeframe of these experiments. The conclusions drawn in Table E-1 might change if the rate of catalyst deactivation were to significantly change after this time.

Both the operation and replacement costs for Carulite catalyst are lower than for the G-43A catalyst suggesting that the former is better for hydrocarbon oxidation. The operating costs of CK-302 and ARI

TABLE E-1. OPTIMUM CATALYST FOR VOC OXIDATION

	Oxidation of		
	Hydrocarbon	Chlorocarbon	Mixed
G-43A	2	-	-
Carulite	1	-	-
ARI	-	1	2
CK-302	-	2	1

v

catalysts for chlorinated stream oxidation were similar. However, the replacement cost of ARI catalyst is only 23 percent of the CK-302 catalyst making ARI the better catalyst for chlorinated stream oxidation. The operating cost of CK-302 catalyst is lower than ARI for the oxidation of mixed stream. The deactivation trend of ARI catalyst for the mixed-stream oxidation suggests the operating costs for this catalyst would rise relatively significantly with time on stream. Thus, the higher replacement cost of CK-302 catalyst would be more than compensated for by its lower operation cost for the oxidation of mixed stream.

H. RECOMMENDATIONS

Future research efforts should be concentrated on developing more reliable analytical methods for HCl and Cl_2 measurements. The results obtained using the Dräger tubes and impinger methods in this work were not very accurate. As a result, the chlorine balance could not be closed. The ability to close the mass balance on chlorine will be very useful in understanding the catalyst deactivation mechanisms.

The use of chromia alumina catalyst in the fluidized-bed reactor for chlorinated stream oxidation results in the loss of chromium from the catalyst. The environmental implications of such chromium loss should be considered from a commercial oxidizer.

This study was conducted using gas stream free of dust and other solid particles which may be present in gas stream from Air Force strippers. The dust and solid particles can cause catalyst deactivation and should be considered for the operation of a commercial oxidizer.

This study was conducted in a laboratory scale reactor. In a commercial reactor using larger particles, significant pore diffusion can occur resulting in reduced conversion. The presence of pore diffusion should be considered for the operation of a commercial scale oxidizer.

PREFACE

Mention of trademarks and trade names of material and equipment does not constitute endorsement or recommendation for use by the Air Force, nor can the report used for advertising the product.

The report has been reviewed by the Public Affairs (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

The technical report has been reviewed and approved for publication.

EDWARD G. MARCHAND, Capt, USAF
Project Officer

ROBERT G. LaPOE, Maj, USAF
Chief, Site Restoration R&D

NEIL J. LAMB, Col, USAF
Chief, Environics Division

FRANK P. GALLAGHER III, Col, USAF
Director, Civil Engineering
Laboratory

The reverse of this page is blank

vii

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF TABLES (CONCLUDED)

The reverse of this page is blank

SECTION I

INTRODUCTION

A. OBJECTIVES

The objectives of this research were to:

- Quantitatively describe the deactivation of commercially available oxidation catalysts used to control volatile organic compound (VOC)-containing gas streams typical of those produced by air-stripping operations.

- Develop a standard test procedure for evaluating catalysts for VOC oxidation.

- Measure the activity and selectivity of these catalysts as a function of time on stream.

- Determine the dominant deactivation mechanisms for two separate classes of VOC-containing waste streams, namely those containing jet fuel components and those containing chlorinated compounds as well as mixtures of these two classes.

- Characterize the chemical and physical properties of commercial catalysts before and after extended, continuous runs at conditions typical of field practice.

- Develop a set of simple mathematical expressions that will describe the overall deactivation of each commercial catalyst tested when used for each of three applications, that is, for streams containing (1) jet fuel components, (2) chlorinated solvents, and (3) a mixture of 1 and 2.

- Recommend catalyst systems most cost-effective for each of the above three applications.

B. BACKGROUND

Catalytic oxidation is a commercially practical method used to oxidize trace contaminants in air (References 1, 2, and 3). A recent application of catalytic oxidation is to control the emission of VOCs from air strippers used to clean the groundwater at various Air Force sites (References 4 and 5). Catalyst deactivation in this application may be caused by coking, fouling by mineral salts in the water, poisoning by various impurities in the water, or sintering and evaporation of the active metal. Depending on the type of catalyst, feed and the reactor configuration, the catalyst can deactivate by any one or a combination of these mechanisms. As the catalyst deactivates, some of the VOCs may pass through the catalyst bed unreacted and/or partially oxidized, that is, both the activity and selectivity may change with time. This is important because the partially oxidized product may be more toxic than the original compound. For example, Weldon and Senkan (Reference 6) observed the formation of Cl_2 in the catalytic oxidation of CH_3Cl over 19 percent Cr_2O_3 on alumina at temperatures from 340 to 470 °C and space

velocities from 2.6 x 10^4 to 3.6 x 10^4 h^{-1}. It is therefore necessary to understand how the catalyst deactivates and to develop methods to predict the deactivation.

Depending on the time scale of deactivation, the catalytic activity can be restored (if not irreversibly poisoned or sintered) in different ways. For example, in fluid catalytic cracking, where the deactivation is very fast, a recirculating reactor is used for continuous catalyst regeneration. However, if the deactivation is slow and if constant conversion is desired to meet certain environmental regulations as in VOC oxidation, the temperature level can be used to compensate for the loss of catalytic activity. Under such conditions, the deactivation effects are measured by the temperature increase required to maintain constant conversion.

C. SCOPE

Table 1 shows typical VOC concentrations at three Air Force Bases. None of these contain only hydrocarbons or only chlorinated compounds; all contain some mixture of the

**TABLE 1. TYPICAL VOC CONTENT OF GAS STREAMS FROM AIR STRIPPERS
AT AIR FORCE BASES**

Compound	Concentration in air, ppm		
	Wurtsmith AFB	McClellan AFB	Hill AFB
Hydrocarbon			
Benzene	9.2	--[a]	0.1-0.25
Pentane	42.4	--	--
Cyclohexane	66.1	--	--
Methyl cyclopentane	7.7	--	--
2,3-dimethyl butane	1.6	--	--
Ethyl benzene	8.3	--	--
Cumene	3.4	--	--
m-,p-xylene	21.3	--	--
Acetone	--	44	--
Toluene	--	--	0.1-0.5
Chlorinated			
Trichloroethylene	17.9	27	--
1,2-dichloroethane	--	--	0.5
1,1-dichloroethane	--	23	--
1,1-dichloroethylene	--	64	--
Vinyl chloride	--	3.5	--
Methylene chloride		11	1-2
Total	177.9	172.5	1.7-3.25

Source: Reference 7.
[a]Not present.

2

two. Since the deactivation processes and types of catalysts to be used are distinctly different if chlorinated compounds are present in the gas stream, this effect was investigated by using gas streams shown in Table 2. Two hydrocarbon catalysts were tested on "jet fuel" stream and two chlorine-resistant catalysts were tested on the "chlorinated solvent" and "mixed" streams. The purpose of this was to provide the Air Force with a deactivation mechanism directly pertinent to the control of air-stripping emissions at specific Air Force Bases.

The catalysts were tested for an extended time using laboratory-scale reactors. The operation was conducted at constant conversion (above 99 percent) in which the catalyst was exposed to gas streams typical of an air-stripper overhead. The temperature was periodically increased to compensate for any decrease in the activity of the catalyst due to deactivation.

The ARI catalyst that was evaluated in this investigation is designed for fluid-bed operation. The physical and chemical deactivation can interact in a fluid-bed reactor. For example, it is possible that attrition may have a positive effect on catalyst activity by constantly exposing fresh catalyst surface. This positive effect would be especially important if deactivation were due to coke formation, which tends to occur on the outer surface of the catalyst (Reference 8). To separate the effects of chemical and chemical/physical deactivation in a fluid bed, the deactivation of the ARI catalyst was

TABLE 2. GAS STREAM COMPOSITIONS STUDIED IN THIS WORK

Compound	Concentration, ppm		
	Jet fuel stream "Stream A"	Chlorinated solvent stream "Stream B"	Mixed stream "Stream C"
Hydrocarbon			
Benzene	29	--[a]	26
n Pentane	132 5	--	119
Cyclohexane	206.5	--	185.5
Methyl cyclopentane	24	--	21.5
2,3-dimethyl butane	5	--	4.5
Ethyl benzene	26	--	23.5
Cumene	10.5	--	9.5
m-,p-xylene	66.5	--	60
Chlorinated hydrocarbons			
Trichloroethylene	--	124	50.5
Methylene chloride	--	50.5	--
1,2-dichloroethane	--	105.5	--
1,1-dichloroethylene	--	220	--
Total	500	500	500

[a]Not present.

3

studied in both fixed- and fluid-bed reactors. The fixed-bed runs allowed study of the deactivation due to chemical mechanism alone (for example, chlorine poisoning, sintering, coking), while the fluid-bed runs allowed study of the combined effects of chemical deactivation and physical attrition/abrasion.

SECTION II

REVIEW OF CATALYST DEACTIVATION

A. BACKGROUND

Deactivation is used to describe a wide range of physical and chemical processes leading to the loss of activity of the catalyst toward the desired reactions, in this case oxidation. These various processes are usually divided into four mechanisms:

- Fouling,
- Poisoning,
- Thermal degradation, and
- Vaporization of active metal(s).

Each of these is usually present to some degree during any application of heterogeneous catalysis, although not all might be significant.

Catalysts usually consist of an active material (a noble metal or metal oxide) dispersed on the surface of a highly porous support, such as alumina oxide. Fouling is the term given to the blockage of these pores which reduces the surface area available to reactants. This plugging can be a physical process involving dust or other fine solid material, or physico-chemical, as is the case with coking. Coke is the term given to large, usually highly aromatic molecules produced via a free radical mechanism under the same conditions as the desired reaction. The polymer-like compound eventually covers active sites on the surface of the catalyst, thereby blocking further reactions. One common cause of coking is high-temperature operation during which thermal decomposition and cracking of the organic reactants lead to its formation.

The poisoning of a catalyst refers to the preferential adsorption of any of a number of chemical species on the active sites of the catalyst, thereby preempting the adsorption of reactants. Even very low levels of some compounds can cause poisoning so that evaluation of this mechanism as a mode of deactivation requires a detailed knowledge of the feed composition. Common poisons that deactivate oxidation catalysts include heavy metals (for example, Pb, Hg, Bi), halogens, and sulfur compounds. Recent research, however, has yielded catalysts relatively resistant to chlorinated compounds.

The thermal degradation of catalysts can involve the deactivation of both active sites as well as the support. At high temperatures (~500 °C), the metal crystals that form the active sites on many catalysts may migrate across the surface, coalescing with other crystals and forming large globules, which reduces the active surface area. This is called sintering. Some supports can also melt at these temperatures leading to the collapse of the pore structure, again resulting in a reduction of surface area. Sintering and pore structure changes represent irreversible damage to the catalyst. Although high temperatures are usually needed to cause such damage, hot spots can develop in

5

commercial systems operating at gas inlet temperatures well below those where thermal degradation might be expected.

Finally, the vaporization of the active metal(s) represents an unavoidable, though usually slow, loss of catalyst activity. This mechanism involves the formation of volatile metal compounds, such as carbonyls, which then vaporize and carry the metals away. As with sintering, this mechanism of deactivation occurs only at relatively high temperatures.

Because all catalysts deactivate over time, it is important for the Air Force to have the best possible understanding of catalyst deactivation so that:

* *The economics of catalyst replacement or regeneration is properly accounted for.* Some deactivation is reversible and some is not. The economics of these two cases may be very different. How can these costs be predicted beforehand?

* *The proper catalyst is chosen for each given gas stream.* Given the likely variability in concentration and VOC chemical type that could be present in gas streams from air stripping at different Air Force Bases, it is important to know how deactivation varies with VOC concentration and type. What is the best catalyst, including the economics of deactivation, for a given air-stripping operation? What types of VOCs (for example, chlorinated ones) are most likely to deactivate a given catalyst?

* *Any change in oxidized product distribution as the catalyst deactivates is understood.* As a catalyst deactivates, the nature of the surface reaction may change, leading to a different range of oxidized products. Whereas HCl may be the initial acidic product of complete oxidation of chlorine compounds (like trichloroethylene), different and perhaps more toxic products like phosgene could be formed as the catalyst deactivates. What happens to a given air-stripper gas stream as it is oxidized over an aged catalyst? Are toxic products formed?

B. DEACTIVATION MODELING

Having determined quantitatively the activity and selectivity of the various catalysts over time and having some insight into the mechanism of deactivation, the data can be used to develop simple mathematical expressions for the deactivation as a function of time. Depending on the dominant mechanism of deactivation, the expressions can have different forms. As one example, coking, which is (often) the reversible deposit of carbonaceous material on a catalyst surface, has been correlated by the simple expression (Reference 9):

$$C_c = At^\eta \tag{1}$$

where C_c = concentration of coke on the catalyst, t is time on stream, and A and η are constants, with η having values typically between 0.5 and 1. Assuming that the concentration of coke is inversely proportional to the catalytic activity, S, then

$$S = \frac{B}{C_c} \tag{2}$$

where B is a constant. Thus,

$$S = \frac{B}{A} t^{-\eta} . \tag{3}$$

If coking were independently confirmed as a deactivation mechanism by, for instance, spectroscopic analysis and if a dependence of activity on time were of a form that could be correlated reasonably well by Equation (2), then Equation (3) could become a means of predicting catalyst life by simply determining the value of B/A and η for different catalysts exhibiting this type of behavior.

As another example, Szepe and Levenspiel (Reference 10) have proposed an equivalent general expression of the form

$$\frac{dS}{dt} = -KS^m \tag{4}$$

to account for deactivation due to catalyst pore blockage, a form of fouling, where again S is the catalyst activity, t is time, and K and m are empirically determined constants. Hughes (Reference 8) summarizes various integrated forms of this expression that have been used to correlate the deactivation of various catalysts.

Having fit an expression like Equation (3) or Equation (4) to the experimental data, the catalyst life can be predicted by determining the minimum acceptable activity, S_{min} (known from the maximum allowable VOC emissions from the catalytic oxidation unit), and solving for t. For instance, if m = 2 in Equation (4), then

$$\frac{1}{S_{min}} = \frac{1}{S_o} + Kt \tag{5}$$

and

7

$$t = \frac{1}{KS_{min}} - \frac{1}{KS} \ . \tag{6}$$

The economics of the catalyst deactivation can be determined by knowing t, and knowing whether the catalyst activity is partially (or totally) regenerable or whether it must be discarded.

The result of catalyst deactivation data analysis is a model which, for given operating conditions, can predict the performance of the catalyst as a function of time. The development of the model is also essential in identifying important control variables, such as the following: (1) What temperature is required for a given conversion? (2) What levels of impurities can be tolerated? (3) What, if any, operating parameters must be monitored to ensure complete conversion?

SECTION III

EXPERIMENTAL

A. CATALYSTS

In an earlier project (EPA Contract 68-02-3767), the Research Triangle Institute (RTI) surveyed all vendors of catalysts for complete oxidation of hydrocarbon-containing gas streams at low temperatures (Reference 11). Samples were obtained and the most active catalyst was determined. This survey was used as a starting point for our selection of catalysts for the jet fuel component air streams. Two different catalysts were selected for the oxidation of jet fuel air streams. For chlorinated air stream oxidation, RTI contacted several vendors, resulting in the selection of two catalysts.

Table 3 summarizes the catalysts studied along with the vendors from which they were obtained. These catalysts belong to two different generic classes: noble metal/metal oxide and mixed-metal oxides. The deactivation mechanisms on these classes of catalysts may be quite different. Any one of these classes of catalysts may be used in commercial systems to control gas streams of interest to the Air Force. For example, the Engelhard Torvex system uses a noble metal/base metal oxide catalyst while the Dedert-Topsoe and ARI catalysts are mixed metal oxides.

Each of the four selected catalysts is commercially used for VOC oxidation. The CK-302 catalyst is being used in a commercial size incinerator, designed for 2000 scfm on a Superfund site in Michigan. This unit is operating on a mixture of 2 g/m^3 chlorinated compounds at a space velocity of 7000 h^{-1}. Because the compounds in the feed stream are not known, the concentration in ppm cannot be determined. Similarly, the three other catalysts are used commercially for the oxidation of VOCs (Reference 12).

TABLE 3. CATALYSTS STUDIED IN THIS WORK

Vendor	Trade name	Formulation	Used for
United Catalysts, Inc.	G-43A	0.1% Pt, 3% Ni/Al$_2$O$_3$	Hydrocarbon stream
Carus Chemical Company	Carulite	Ce/Cu/MnO$_2$	Hydrocarbon stream
ARI Technologies, Inc.	EconAbator	Cr$_2$O$_3$/Al$_2$O$_3$	Chlorocarbon and mixed streams
Dedert Topsoe	CK-302	Mixed-metal oxide[a]	Chlorocarbon and mixed streams

[a] Proprietary catalyst

9

The ARI and Carulite catalysts were obtained in the form of 1/16th inch pellets, while the CK-302 and G-43A catalysts were obtained in the form of 1/4 inch pellets. These pellets were crushed with a mortar and pestle and sieved to obtain the appropriate particle size (35/42, 60/80 or 80/115 mesh). Some 60/80 mesh size quartz particles were also produced by crushing a quartz tube. The particle size for each catalyst was selected to allow laboratory-scale operation at vendor-recommended conditions, representing a compromise between pressure drop and diffusion limitations.

B. CHARACTERIZATION

The catalysts investigated in this study were characterized using a number of techniques, i.e., BET surface area, pore size distribution, elemental analysis, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS).

- BET Surface Area

  The BET surface area of the catalysts was determined by N_2 physisorption at -196 °C using a Quantasorb unit.

- Pore Size Distribution

  The pore size distribution in the catalysts was determined by mercury porosimeter. A Micromeritics Mercury Porosimeter Model Autopore II 9220 was used for this purpose. Pore sizes down to 10 nm were measured.

- Elemental Analysis

  An Instrumentation Laboratory Plasma-100 emission spectrometer was used to determine the bulk chromium content of the fresh and used ARI catalysts.

- X-ray Diffraction

  Structural analysis of the catalysts was performed by the use of powder diffraction. An XRD diffractometer utilizing Cu Kα radiation ($\lambda = 1.5418$ Å) was used for the X-ray diffraction measurements. Powder samples were used for this purpose. Each sample was scanned from $2\theta = 10$ to 60° at a rate of 2°/minute.

- X-ray Photoelectron Spectroscopy

  To gain more understanding of the surface chemistry, the catalysts were studied by XPS, a surface sensitive technique capable of analyzing the uppermost layers (20 to 50 Å) in terms of oxidation states and surface composition. The XPS data were collected on a surface analysis system at Northwestern University. A personal computer (PC) was connected to the spectrometer through a digital-analog interface for collecting and analyzing the data. Powder samples were pressed onto a indium foil which was attached to a stub using Ag

paint to relieve charging of the samples. The sample was introduced into the spectrometer chamber, outgassed at room temperature to a pressure of 10^{-8} torr, and analyzed using a Mg K_α 300 watt source. The experimental spectra were collected for 30 minutes to 2 hours, depending on the peak intensities. The contaminant C 1s peak at 284.6 eV binding energy value was used as a reference to find the binding energies for each element.

C. FEED STREAMS

Three different feed streams were used in this study. The first was generated from a feed gas containing 1000 ppm of C_5 to C_9 hydrocarbon compounds which was blended with an equal volume of VOC-free air saturated with water vapor. The humidified air was generated by passing the VOC-free air through a water bubbler maintained at room temperature. The resulting Stream A thus contained 500 ppm of hydrocarbons and had a dew point of 59 °F (1.6×10^4 ppm H_2O). Stream B was generated in the same way and contained 500 ppm of C_1 to C_2 chlorinated hydrocarbons. Stream C was also generated in the same way and contained 450 ppm of C_5 to C_9 hydrocarbons plus 50 ppm of trichloroethylene. The compositions of the three streams are summarized in Table 4. Some experiments were also conducted using 200 ppm VOC feed streams produced in the same way as the 500 ppm feed stream.

TABLE 4. FEED STREAMS COMPOSITION IN PARTS PER MILLION

Compound	Stream A	Stream B	Stream C
Pentane	132.5	--[a]	119
2,3-Dimethylbutane	5	--	4.5
Methyl cyclopentane	24	--	21.5
Cyclohexane	206.5	--	185.5
Benzene	29	--	26
Ethyl benzene	26	--	23.5
m,p-Xylene	66.5	--	60
Cumene	10.5	--	9.5
Trichloroethylene	--	124	50.5
Methylene chloride	--	50.5	--
1,2-Dichloroethane	--	105.5	--
1,1-Dichloroethene	--	220	--
Water vapor	1.6×10^4	1.6×10^4	1.6×10^4
Total (moisture free)	500	500	500

[a] Not present.

11

The VOC-containing air was obtained from Scott Specialty Gases (Plumstedville, PA). In addition to the four chlorinated compounds (methylene chloride, 1,1-dichloroethylene, 1,2-dichloroethane, and trichloroethylene), the gas cylinders supplied by Scott had some impurities such as chloroform, 1,1,2-trichloroethane, 1,1,1,2-tetrachloroethane, and 1,1,2-trichloropropene. These impurities were determined using the gas chromatography-mass spectrometry (GC-MS) facility at RTI. The concentration of each of these impurities was less than 1 ppm in the feed stream.

Due to vapor pressure limitations, cylinders containing hydrocarbons and mixed stream could be pressurized to only 300 psig. The cylinder containing chlorocarbons could be pressurized to 1,500 psig. This resulted in a significantly reduced amount of gas in the cylinder and increased the number of cylinders used. Twenty gas cylinders were initially ordered from Scott (nine each of hydrocarbons and chlorocarbons and two of mixed compounds). Once these cylinders were consumed, additional gases were made at RTI. RTI has a facility to prepare premixed gases on a routine basis. The chlorocarbons containing air, prepared at this facility, had significantly reduced impurities compared to those obtained from Scott.

D. REACTOR SYSTEM

Four fixed-bed and two fluid-bed laboratory scale reactors were used to study the catalyst deactivation for VOC oxidation. The reactors were operated continuously at atmospheric pressure. Figure 1 shows the schematic diagram of the reactor system used in this study. The fixed-bed reactor consisted of a 4-mm i.d. and 40-cm length quartz tube. The catalyst was held in place by a small plug of quartz wool. Approximately 15 cm of the 4-mm i.d. tube served as a preheating zone. A small amount of quartz pieces was placed above the catalyst on the upstream side to provide a uniform gas flow. The fluid-bed reactor used for the oxidation of chlorinated stream consisted of a 1-cm i.d. quartz tube fused onto a 0.8-cm o.d. tube. The 1-cm i.d. tube had a fritted disc on which the catalyst was supported. The catalyst supported on the disc corresponded to the middle of the heated zone of the furnace. The fluid-bed reactor used for the oxidation of the mixed stream was similar to the fluid-bed reactor used for the chlorinated stream except that it had a 0.7-cm i.d. tube fused to a 0.4-cm tube. The catalyst was placed on a quartz frit in the 0.7-cm tube. Each reactor was heated in a tube furnace to the reaction temperature which was controlled to ± 1 °C by Omega CN-9000 temperature controllers. The reactor inlet temperature was measured by a $1/16^{th}$ inch inconel-sheathed thermocouple mounted inside the reactor on the feed side.

Teflon® tubings and fittings were used in the system to avoid corrosion from chlorine-containing compounds. Also, the tubing downstream of the reactor was heated to about 70 °C to prevent condensation. Similarly, the thermocouples were placed on the feed side and inconel-sheathed to minimize the corrosion from HCl. The valves used in the GC were also made of inconel.
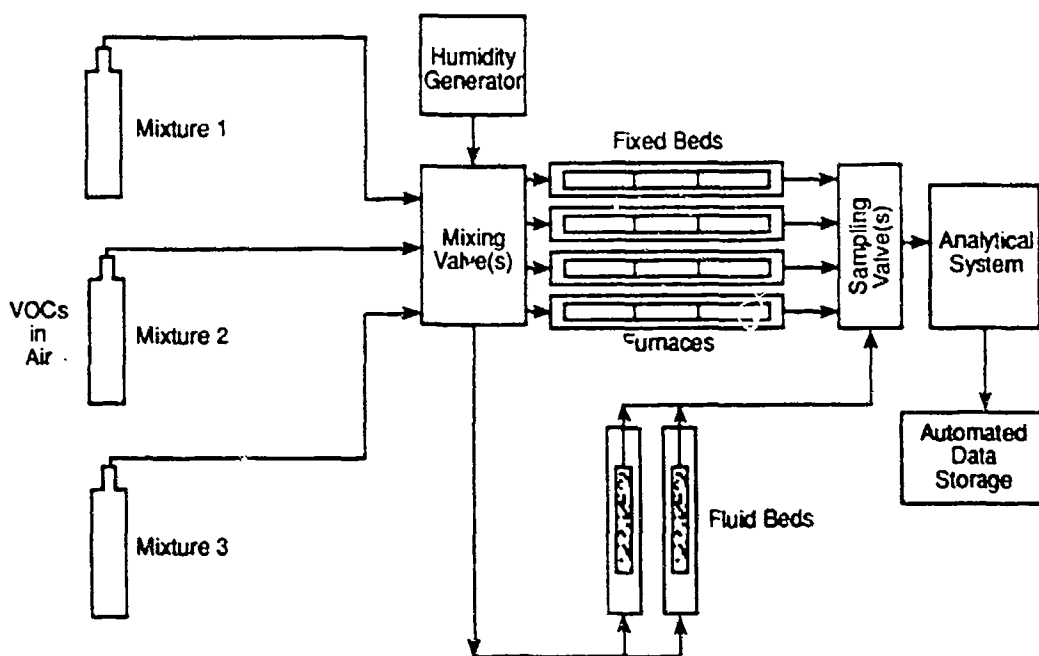
Figure 1. Schematic of a Reactor System

The effluent stream from each reactor was passed continuously through a three-port solenoid valve and vented through a fume hood to the atmosphere. The valve position could be changed by a programmable Chrontrol® and the effluent stream could be directed to the GC through an eight-port manifold. All the reactor effluents were fed to the GC through this manifold. Thus, any one reactor effluent could be analyzed at a time. The Chrontrol® could be programmed for periodic switching of the solenoid valves. This allowed the continuous effluent analysis without any supervision.

The validity of the data collected from a continuous reactor is jeopardized if a power failure causes the run to stop. This was anticipated in the experimental setup by using a three-way solenoid valve used for each reactor. In the event of a power failure, the solenoid valve allowed the flow of inert gas (nitrogen) over the catalyst. A timer was used to lock out the system if the power failure was above a certain time (lock-out time). If the time during which the power was off was less than the lock-out time, the system started automatically on return of power. However, if the power failure was for greater than the lock-out time, the system remained shut off with the inert gas flowing continuously over the catalyst. This arrangement was necessary for operating the temperature controllers smoothly and preventing the moisture and VOC from contacting the catalyst at low temperatures. In this situation, the system had to be started manually.

The lock-out time was initially set at 1 minute. On April 2, 1990, an electrical storm caused a power failure in the building. An Omega data logger was connected to a circuit

13

in which the voltage dropped to 70 volts a.c. for a period of 1 minute (until the lock-out feature was activated). When power was restored manually, sparks and then smoke were observed coming from the data logger. The power to the data logger was disconnected. The damage to the data logger was probably caused by the voltage remaining for a long time (1 minute). As a result, the lock-out time was reduced to 15 seconds. The data logger was repaired and used for the remainder of the study.

E. ANALYTICAL SYSTEM

An on-line analysis of the effluent gases was conducted using a gas chromatograph (Hewlett Packard model 5890 Series II). The GC was equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) and a temperature programming mode was used to analyze the feed gases as well as the effluent stream. The effluent gases were analyzed for the unconverted VOCs, partial oxidation products such as chloroform and 1,1,2-trichloroethane, and total oxidation products (CO and CO_2). The FID was used for the hydrocarbon analysis, while the TCD was used for carbon monoxide and carbon dioxide analyses. A DB-624 fused silica capillary column was used for the hydrocarbon separation. The carbon monoxide and carbon dioxide were separated using molecular sieves (5A) and Hayesep R columns. Linearity tests of the FID for all the VOCs showed good linearity across the concentrations varying by a factor of 100. The composition of the gas stream was determined from the peak areas of the resulting chromatograph. The peak areas were calculated by a Hewlett Packard 3396A Integrator. The response factors were calibrated using gas stream of known composition.

A short BASIC program was written to automate the GC analysis. This program was capable of loading appropriate GC methods for analysis, injecting the sample and calculating the gas composition. The program was able to conduct the analysis at any predetermined time which coincided with the Chrontrol programming. Generally, all the reactor effluents were analyzed once a day.

The chlorine and hydrogen chloride analyses were conducted using Dräger tubes because development of GC methods and wet chemical techniques using impingers for quantitative analysis of hydrogen chloride and chlorine was unsuccessful. Hayesep R column, recommended by both Supelco and Alltech for separation of hydrogen chloride, chlorine, and nitrogen, was initially used. A 500-ppm chlorine in dry nitrogen standard was analyzed under a variety of GC conditions, but no peaks corresponding to the expected retention time for chlorine were observed. Similarly, when the effluent gases from the CK-302 catalyst, containing HCl and Cl_2, were passed into the GC, a large water peak was detected by the TCD, but no peaks corresponding to HCl or Cl_2 were observed. When the air humidifier was bypassed, a small water peak (from the oxidation of the chlorinated hydrocarbons) was observed along with a second peak which could correspond to HCl or Cl_2. When the humidified air was resumed and more measurements were made, the second peak was not observed, and Dräger tube measurements of the GC sample vent gas indicated that no HCl was present.

14

Based on the likely reaction of HCl with metal surfaces in the GC sample flow path in the presence of high moisture levels, quantitative analysis of hydrogen chloride or chlorine by gas chromatography was assumed to be not feasible. Alternate wet chemical techniques involving impinger sampling with analysis by ion chromatography was also investigated. This allowed sampling directly at the reactor outlet and improved the chances for quantitative measurement of HCl and Cl_2 produced in the reactor. A series of two impingers was used and connected close to the reactor exit to minimize any adsorption of chloro-compounds. The first impinger contained 25 cc of 0.1 N sulfuric acid and the second contained 25 cc of 0.1 N sodium hydroxide. The effluent gases were passed through the impingers for 15 minutes and the solutions were sent for chlorine analysis by ion chromatography at a different RTI facility. Because chlorine has very low solubility in an acid medium, only hydrogen chloride dissolves in the sulfuric acid. The chlorine in the effluent gas then dissolves in the sodium hydroxide. Knowing the total gas flow to the impingers and the chlorine content by ion chromatography, the HCl and Cl_2 concentration in the effluent were calculated.

The results obtained from impinger analysis were in serious error. For example, some of the sample solutions were found to contain less chlorine than the blank solution. Because of the failure of GC and impinger techniques, Dräger tubes were used for HCl and Cl_2 analysis. Dräger tube analysis is believed to be ± 30 percent in error.

F. DATA ACQUISITION

A PC was connected to the integrator using a digital-analog interface (RS-232-C link). A BASIC program obtained from Hewlett-Packard was used to communicate between the PC and the integrator. This arrangement allowed the raw data to be collected on the computer hard disk. The raw data from each run were stored in a separate file. A FORTRAN program was written to read the raw data from these files, calculate the conversions for individual components and the total conversion, and save the output in a new file. These data were then imported into a Lotus spreadsheet for deactivation analysis. The reactor temperatures were manually incorporated in the spreadsheet.

G. CALCULATIONS

The conversion was calculated on the basis of total carbon atoms in the feed.

$$\text{Total conversion} = X_t = \frac{\Sigma C_I - \Sigma C_o}{\Sigma C_I} \times 100 \qquad (7)$$

where:

X_t = percentage total conversion based on carbon atoms
ΣC_I = sum of all the carbon atoms in the compounds at the inlet
$\Sigma C'_o$ = sum of all the carbon atoms in all the compounds (except CO and CO_2) in the effluent;

15

The conversion of individual compounds is calculated as follows:

$$X_n = \frac{C_I - C_o}{C_I} \times 100$$

(8)

where

X_n = percentage conversion of component n

C_i^n = inlet concentration of component n

C_o = outlet concentration of component n.

SECTION IV

RESULTS AND DISCUSSION

A. CHARACTERIZATION

The catalysts were characterized by BET surface area, porosity, and XRD. Table 5 summarizes the surface area and average pore diameter for the catalysts investigated in this work. The diffraction pattern of the ARI catalyst indicated γ-Al_2O_3 phase; however, the diffraction patterns of other catalysts did not show peaks suggesting the presence of amorphous or highly dispersed phases.

B. GAS PHASE OXIDATION

Blank reactor runs were conducted to determine the extent of oxidation of hydrocarbons (Stream A) and chlorocarbons (Stream B) at the elevated temperatures expected at the end of the long-term runs. These runs are a part of the protocol for all catalytic studies because they are used to account for the effect of the catalyst itself in carrying out the reaction. The results are summarized in Tables 6 and 7.

All runs were made at 50 cc/min total flow with 25 cc/min of air saturated with water vapor at 20 °C, 25 cc/minute of premixed gases, and a "blank" reactor containing all elements that will be in the reactor during long-term runs except the catalyst (that is, thermocouple, quartz wool, and quartz chips). The resulting feed stream had a VOC concentration of 500 ppm. The results show that, for the "blank reactor" runs at least, the hydrocarbons are more reactive than the chlorinated compounds, as expected. The rather low apparent activation energies suggest some surface initiated reaction is taking place even in the absence of a catalyst, perhaps by interaction of the quartz and water vapor.

C. PRELIMINARY CATALYTIC RUNS

Some preliminary runs were conducted using 200 ppm VOC concentration gas streams. These runs were conducted to investigate the effect of temperature and space velocity on the VOC conversions. It should be noted that the long-term runs were conducted using 500 ppm VOC concentration.

1. G-43A Catalyst

Preliminary experiments were conducted to study the effect of temperature and space velocity on the conversion and test the presence of mass transport limitations. The effect of temperature on the activity of the G-43A catalyst for the different hydrocarbons oxidation is shown in Table 8. In the temperature range studied, the conversion of all aromatics (benzene, ethyl benzene, meta and para-xylene, and cumene) was greater than

17

TABLE 5. BET SURFACE AREA AND PORE VOLUME OF FRESH CATALYSTS

Catalyst	Surface area m²/g	Pore volume cc/g	Average pore diameter, nm
G-43A	248	0.46	7.4
Carulite	132	0.37	11.2
CK-302	167	0.26	6.1
ARI	188	--	--

TABLE 6. GAS PHASE CONVERSION OF A STREAM, NO CATALYST

Hydrocarbons	Temperature, °C				Apparent activation energy, kcal/mol
	453	502	558	602	
Pentane	0.4	0.4	1.4	3.7	20
2,3-Dimethyl butane	0.5	0.5	0.4	0	--
Methylcyclopentane	0.2	0.2	2.7	7.2	29
Cyclohexane	0.2	0.2	2.9	8.1	30
Benzene	0	0	0	0	--
Ethyl benzene	3.3	6.8	19.2	37.0	21
m,p-Xylene	3.0	6.2	19.7	39.0	22
Cumene	3.1	5.6	20.1	37.3	21
Overall	1.1	2.5	7.5	15.9	23

TABLE 7. GAS PHASE CONVERSION OF B STREAM, NO CATALYST

Chlorocarbons	Temperature, °C						Apparent activation energy, kcal/mol
	353	402	454	503	552	604	
1,2-Dichloroethane	0	0	0	0	0	0.7	0
Methylene chloride	0	0	0	0.5	0	0	0
1,1-Dichloroethylene	0	0.1	0.5	2.5	7.1	23.7	30
Trichloroethylene	0	0	0	0	0	2.4	0
Overall	0	0	0	0.1	1.4	6.7	43

18

TABLE 8. HYDROCARBONS CONVERSIONS OVER G-43A CATALYST

Temperature (°C)	275	300	325	350	375	400
n-Pentane	10.7	23.4	41.2	65.4	85.9	97.4
2,3-Dimethyl butane	21	46.9	70.9	90.4	97.1	>99.9
Methylcyclopentane	46.8	76.8	92.7	98.9	>99.9	>99.9
Cyclohexane	43.4	73.6	91.1	98.7	>99.9	>99.9
Benzene	94.1	95.1	96.2	98.3	>99.9	>99.9
Ethyl benzene	99.8	99.8	>99.9	>99.9	>99.9	>99.9
m,p-Xylene	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
Cumene	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
Total conversion	54.3	70.8	82.7	91.6	96.9	99.4

Inlet concentration = 200 ppm total hydrocarbon, water concentration
corresponding to a dew point of 70 °F
Total flow = 50 cc/min
Space velocity = 9950 h^{-1}
Particle size = 80/115 mesh

94 percent. Furthermore, except for benzene, the conversions of the three aromatics were essentially complete in the 275 to 400 °C range, suggesting that the rate is limited by external diffusion for the oxidation of aromatic compounds. The conversions for the nonaromatic compounds were a sharp function of temperature. The apparent activation energies, calculated assuming first-order kinetics, were close to the activation energies for the oxidation in the gas phase. This suggests the absence of external mass transport limitations for the nonaromatic compounds. The absence of external mass transport limitations for the nonaromatic compounds was further tested by changing both the flow and catalyst bed height to keep the space velocity constant. These results are summarized in Table 9. The conversions for the nonaromatic compounds were similar at two different flow rates, confirming the absence of external diffusion limitations under these conditions.

The effect of space velocity (space velocity = total gas flow rate/catalyst volume) on the conversions at 325 °C over G-43A catalyst is shown in Table 10. As expected, the conversions decreased with an increase in space velocity. Again, the aromatics conversions (except benzene) were independent of the contact time.

2. Carulite Catalyst

The effect of temperature on the activity of the Carulite catalyst was investigated. This catalyst exhibited complete hydrocarbon conversion above 300 °C. However,

19

TABLE 9. EFFECT OF GAS FLOW RATE AT CONSTANT SPACE VELOCITY ON HYDROCARBON CONVERSION OVER G-43A CATALYST

Flow (cc/min)	Bed height (cm)	n-Pentane	2,3-Dimethyl butane	Methyl-cyclopentane	Cyclohexane	Benzene	Ethyl benzene	m,p-Xylene	Cumene	Total conversion
25	0.6	46.1	74.1	91.3	90.3	98.8	>99.9	>99.9	>99.9	83.5
100	2.4	47	76.7	93.6	92.3	98.1	>99.9	>99.9	>99.9	84.6

Total concentration = 200 ppm total hydrocarbon, water concentration approximately 2×10^4 ppm
Particle size = 80/115 mesh
Temperature = 325 °C

TABLE 10. EFFECT OF SPACE VELOCITY ON THE HYDROCARBON CONVERSIONS OVER G-43A CATALYST

Flow (cc/min)	Space velocity h^{-1}	n-Pentane	2,3-Dimethyl butane	Methyl-cyclopentane	Cyclohexane	Benzene	Ethyl benzene	m,p-Xylene	Cumene	Total conversion
20	4,000	70	93.8	99.5	99.4	99.2	>99.9	>99.9	>99.9	93
40	8,000	50.7	80.5	96.8	95.7	95.8	>99.9	>99.9	>99.9	86.9
50	10,000	41.2	70.9	92.7	91.1	96.3	>99.9	>99.9	>99.9	82.7
100	20,000	33.8	58.5	84.5	82.4	93.5	>99.9	>99.9	>99.9	76.9

Total concentration = 200 ppm total hydrocarbons, water concentration approximately 2×10^4 ppm
Temperature = 325 °C
Particle size = 80/115 mesh

20

significant loss of catalyst activity was observed when the catalyst was operated at lower temperatures for extended periods. The original activity was restored upon heating the catalyst above 300 °C. The loss in catalyst activity at low temperatures may be due to adsorption of hydrocarbons forming coke on the surface or due to adsorbed water vapor. Because of the loss in activity below 300 °C and complete conversion above 300 °C, no meaningful conversion data could be obtained over this catalyst.

3. CK-302 Catalyst

The conversions of chlorinated hydrocarbons over the CK-302 catalyst at 300 and 350 °C are shown in Table 11. The overall carbon conversion was 99.5 percent at 350 °C. This catalyst also exhibited loss in activity if kept at low temperatures for extended periods.

4. ARI Catalyst

The activity of the ARI catalyst as a function of temperature for chlorinated hydrocarbons oxidation is summarized in Table 12. The conversion of methylene chloride was low at all temperatures compared to the conversions of C_2 chlorocarbons. The apparent activation energies were in the 20 to 25 kcal/mol range, indicating the absence of external mass transport limitations.

D. LONG-TERM DEACTIVATION RUNS

Four catalysts were investigated for oxidation of three different feed streams for an extended period of time. The ARI catalyst was tested in both fixed-bed and fluid-bed reactors. The reaction conditions for the deactivation runs are summarized in Table 13. The initial temperatures and the space velocities were the same as those recommended by the catalyst vendors. The recommended startup temperature for the CK-302 catalyst is 350 °C. However, since considerable partial oxidation products were formed over CK-302 catalyst for chlorinated stream oxidation, the temperature was increased to 400 °C to maintain total conversion above 99 percent. The particle size was chosen as a compromise between pressure drop and diffusion limitations. Smaller particles are desired to minimize internal diffusion limitations. When particle sizes smaller than that shown in Table 13 were used, considerable pressure drop was observed. The deactivation runs were made at a total inlet VOC concentration of 500 ppm and water vapor concentration corresponding to a dew point of 59 °F. This water vapor concentration is typical of streams from air strippers. This is important because water vapor concentration may affect the deactivation process and it is best to measure long-term deactivation at conditions of practical interest.

1. G-43A Catalyst

The activity as a function of time for the hydrocarbon oxidation over UCI G-43A catalyst is summarized in Table A-1 in Appendix A. The catalyst was on stream for 249 days

TABLE 11. CHLORINATED HYDROCARBON CONVERSIONS OVER CK-302 CATALYST

Temperature (°C)	1,1-Dichloro-ethylene	Methylene chloride	1,2-Dichloro-ethane	Trichloro-ethylene	Total conversion
300	8.1	41.4	84.1	98	70.1
350	98.5	96.8	>99.9	>99.9	99.5

Inlet concentration = 200 ppm total chlorocarbons, water concentration 2 x 10^4 ppm
Particle size = 35/42 mesh
Space velocity = 2940 h^{-1}
Total flow   = 50 cc/min

TABLE 12. CONVERSIONS OF CHLOROHYDROCARBONS OVER ARI CATALYST IN FIXED-BED REACTOR

Temperature (°C)	1,1-Dichloro-ethylene	Methylene chloride	1,2-Dichloro-ethane	Trichloro-ethylene	Total conversion
359	>99.9	75.0	96.1	>99.9	97.5
282	91.9	40.7	74.5	>99.9	88.9
266	68.3	23.0	55.8	99.4	77.7
252	48.6	13.2	37.1	94.9	65.9
237	29.6	7.0	22.9	78.3	49.9

Total flow = 40 cc/min   Particle size = 100/115 mesh
Space velocity = 23,970 h^{-1} Inlet concentration = 200 ppm

TABLE 13. REACTION CONDITIONS FOR LONG-TERM DEACTIVATION RUNS

Catalyst	Stream	Particle size, mesh	Space velocity*, h^{-1}	Initial temperature °C	Particle size, μ
UCI	Hydrocarbon	80/115	9,500	430	150
Carus	Hydrocarbon	60/80	15,000	315	210
CK302	Chlorocarbon	35/42	3,700	400	384
CK302	Mixed	35/42	3,700	350	384
ARI	Chlorocarbon	60/80	12,000	350	210
ARI (fluid)	Chlorocarbon	60/80	12,000^b	360	210
ARI (fluid)	Mixed	60/80	12,000^b	385	210

Inlet VOC concentration = 500 ppm
Water vapor concentration = 1.6 x 10^4 ppm
* at 1 atmosphere and 32 °F
^{b} for static bed

22

and did not exhibit any loss in activity for the entire duration. The overall carbon conversion was above 99 percent. Also, the conversion of individual compounds was greater than 99 percent during the entire time on stream. Since the catalyst did not suffer any deactivation, the temperature was maintained at 430 °C during the entire time on stream.

No incomplete combustion products were observed over the G-43A catalyst. The only oxidation product was CO_2 and carbon balance was within ± 5 percent at all times.

The activity tests were terminated after 249 days (5,976 hours) on stream. The catalyst was cooled to room temperature in a nitrogen (inert) stream. The catalyst bed exhibited various black spots, as shown in Figure 2. This is believed to be caused by formation of a carbide phase which is the active phase for oxidation reaction. Similar results were observed in an earlier VOC oxidation study, using this catalyst, conducted by RTI for the U.S. Environmental Protection Agency (EPA) (Reference 13).
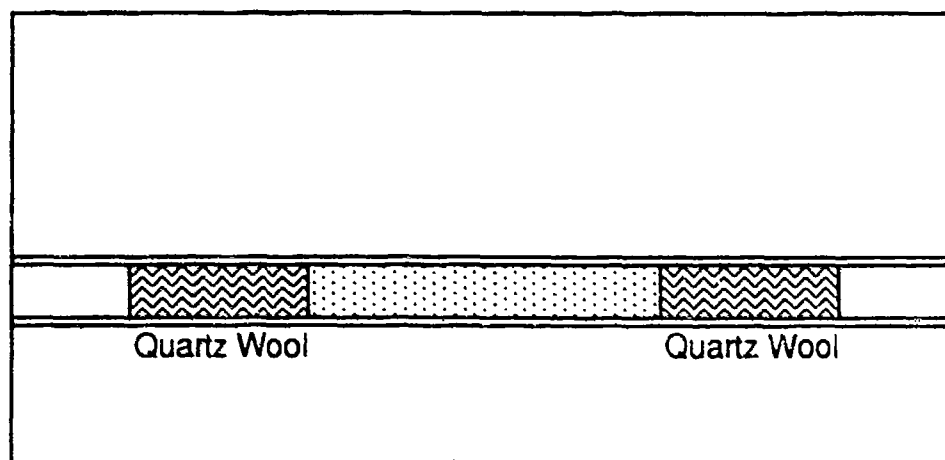
Figure 2. Schematic of Used UCI Catalyst after 249 Days on Stream

2. Carulite Catalyst

The Carulite catalyst was used to oxidize the hydrocarbon stream in a fixed-bed reactor. The catalyst was on stream for 297 days and suffered considerable deactivation.

23

The total conversion was kept constant above 99 percent by periodically increasing the temperature to compensate for the loss of intrinsic catalytic activity. Table A-2 in Appendix A summarizes the activity data as a function of time on stream for hydrocarbon stream oxidation over the Carulite catalyst. The initial temperature was 315 °C based on the preliminary catalytic runs. The temperature was increased to 400 °C over 297 days to keep the total conversion above 99 percent. This corresponds to a temperature increase of 0.29 °C/day. The temperature increase required to maintain constant conversion is shown in Figure 3. A sharp loss in activity, as seen by the increase in catalyst temperature required to maintain total conversion above 99 percent, is observed after 225 days on stream.

The conversion of all compounds, except pentane and benzene, was close to 99 percent. The total conversion was close to 99.9 percent at the start of the run. As the catalyst started deactivating, the conversion dropped below 99.9 percent. The temperature was increased when the total conversion dropped below 99 percent. The conversion of pentane was about 98 percent and the conversion of benzene was about 90 to 95 percent during the entire time on stream. This is shown in Figure 4. The effluent stream over the Carulite catalyst did not contain any partial oxidation products. The only deep oxidation product was CO_2 and the carbon balance was within ± 5 percent.

It is interesting to note that the conversion of benzene decreased significantly with time on stream from 99.9 percent at the start of the run to about 90 percent in 297 days on stream. Most of this decrease was in the first 200 days on stream. Since the concentration of benzene in the feed stream was low (5.8 percent of the total organic compounds), the overall conversion decreased only marginally and was at or above 99 percent at all times (the total conversion at the start of the run was 99.9 percent). Also, of all the hydrocarbons, only benzene and pentane conversions were below 99 percent. Table 8 shows that pentane is the most difficult compound to oxidize over fresh Pt/Ni catalyst and that the catalytic activity for the oxidation of benzene is relatively high. In fact, the conversion of benzene was higher than any of the nonaromatics at all temperatures investigated in this work. Similar results may be expected over fresh hopcalite catalyst. Note that such low conversion tests could not be conducted over hopcalite because of activity loss below 300 °C. The decrease in benzene conversion with time on stream during long-term hopcalite deactivation test suggests that the catalyst is losing activity mainly for the oxidation of benzene. It can be concluded that benzene, in a mixture of nine hydrocarbons, is not the most difficult to oxidize over fresh hopcalite; however, the catalyst activity for benzene oxidation decreases significantly when used for a long period of time.

Various studies have investigated the hopcalite catalyst for the oxidation of organic compounds. The activity and selectivity of hopcalite are affected by certain compounds. For example, oxidation of thiophene over hopcalite causes a gradual loss in catalyst activity (Reference 14). This loss in activity is also accompanied by an increased CO selectivity. Our studies suggest that benzene is one such compound that affects the activity of the hopcalite catalyst. However, no selectivity changes were observed over this catalyst in our

24
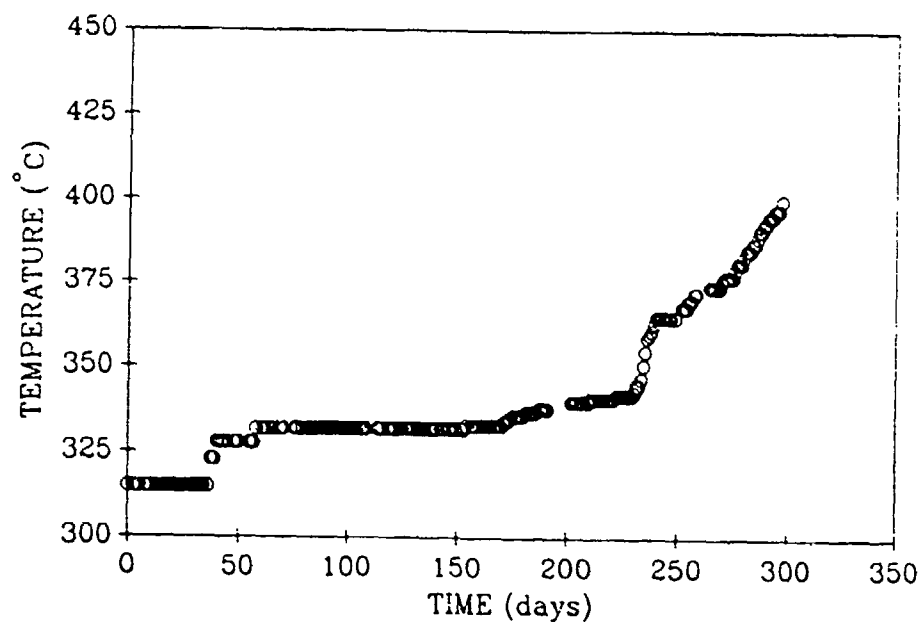
Figure 3. Temperature Increase Required to Maintain Total Conversion Above 99 Percent over Carulite Catalyst
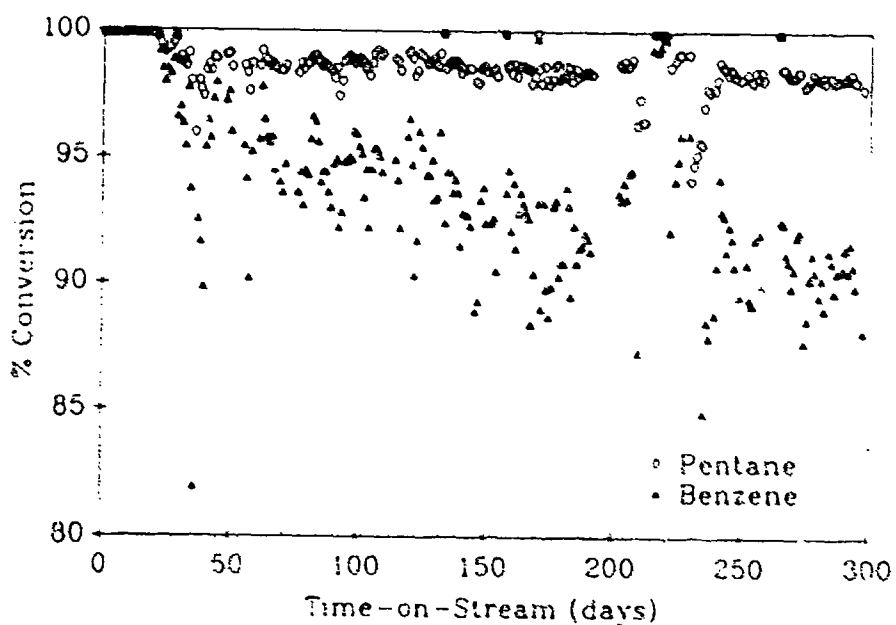
Figure 4. Conversions of Pentane and Benzene over the Carulite Catalyst Used for the Oxidation of Hydrocarbon Stream

25

studies. It is important to emphasize that the decrease in catalyst activity and benzene conversion was observed when the catalyst was used to oxidize a mixture of nine C_5-C_9 hydrocarbons including benzene. Many studies have reported the existence of mixture effects over the hopcalite catalyst (that is, the activity of hopcalite toward certain compound is less when it is exposed simultaneously than it is when it is exposed separately) (Reference 14). Similar mixture effects were observed in our earlier work over the Pt/Ni catalyst when used for the oxidation of n-hexane, benzene and binary mixture (Reference 13). Complete conversion was observed at around 350 °C for 410 ppm n-hexane in dry air and at much lower temperature (near 220 °C), and for 375 ppm benzene in dry air, both at a weight hourly space velocity (WHSV) of 209 h^{-1} (approximately 1.75 x 10^{5}h^{-1} gas hourly space velocity [GHSV]). However, n-hexane oxidation was significantly inhibited by the presence of benzene, though benzene oxidation was not inhibited by the presence of n-hexane. Such mixture effects may be occurring in the oxidation of multicomponent hydrocarbon mixture over the hopcalite catalyst in this study. It also appears that the hydrocarbon mixture used in this study mainly affects the catalyst activity for benzene.

Attempts were made to understand the reasc s for the deactivation of hopcalite catalyst. After 297 days on stream, the catalyst was cooled in nitrogen and the bed was split into three sections: top, center, and bottom. These sections were studied by XPS Table 14 summarizes the Mn 2p and O 1s binding energies in the fresh and used Carus catalyst. The results did not show any significant differences in the Mn 2p binding energies of the fresh and any of the used catalyst sections. Differences were observed in the O 1s binding energy peak. For example, the O 1s binding energy peak of the top section of the used catalyst could be deconvoluted into three peaks. The O 1s binding energy region of the fresh catalyst exhibited only a single peak, while that of the center and bottom sections of the used catalyst showed two peaks. This change in the O 1s spectra suggests some change in the state of manganese oxide species not revealed in the Mn 2p spectra.

3. CK-302 Catalyst

The CK-302 catalyst was tested for the oxidation of both chlorinated and mixed streams in fixed-bed reactors.

a. Chlorinated Stream

The catalyst used for the chlorinated stream did not suffer any deactivation when used for 247 days on stream as shown in Table A-3 in Appendix A. The initial temperature ' 400 °C was maintained for the entire period to obtain total conversion above 99 percent. This initial temperature was slightly greater than the recommended temperature of 350 °C. This is because significant amounts of incomplete combustion products such as 1,1,2-trichloroethane were observed at temperatures below 400 °C. The 1,1,2-trichloroethane was formed even at 400 °C. Generally, the amount was less than 2 ppm in the effluent as

TABLE 14. XPS RESULTS OVER CARUS CATALYSTS

Catalyst	Binding energy, eV		
	Mn 2p$_{1/2}$	Mn 2p$_{3/2}$	O 1s
Fresh	652.9	641.3	531.1
Used			
Bottom	652.6	641.2	532.3, 530.3, 528.3, 526.4
Center	653.6	641.8	530.9, 527.5
Top	653.1	641.5	530.5, 527.3, 525.3

shown in Figure 5. Toward the end of the run, the concentration of 1,1,2-trichloroethane increased to about 4 ppm. In addition to 1,1,2-trichloroethane, trace quantities of chloroform were also formed over this catalyst.

The only deep oxidation product was CO_2 and the carbon conversion was within ±5 percent. In addition to carbon balance, attempts were also made to close the chlorine balance. A chlorine balance is important in studying catalyst deactivation by adsorption of any chlorine-containing compounds. Furthermore, the ratio of chlorine to hydrogen chloride produced over the catalyst provides information about the oxidation activity and the chemical
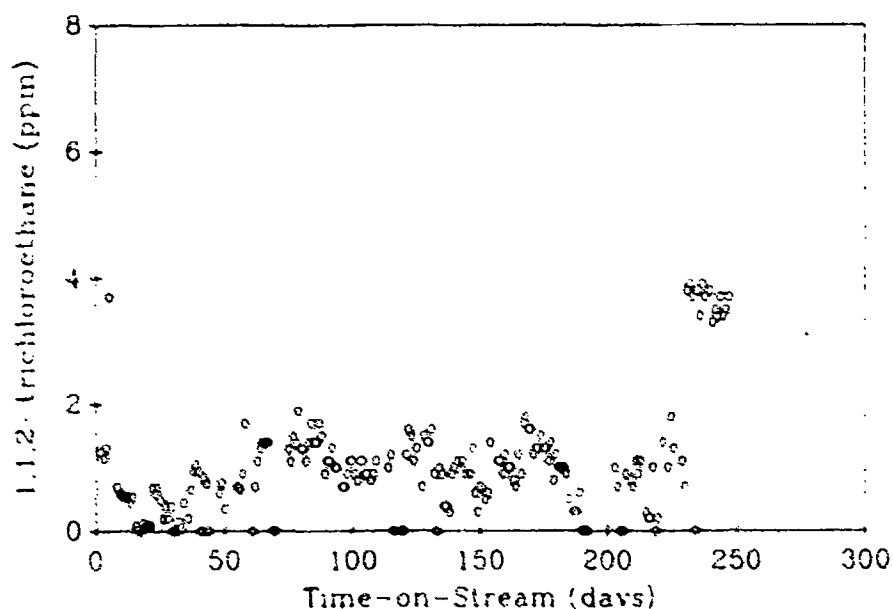
Figure 5. Concentration of 1,1,2-trichloroethane in the Effluent Stream for Chlorinated Stream Oxidation over CK-302 Catalyst

27

properties of the catalyst. The GC methods were unsuccessful for quantitative analysis of hydrogen chloride and chlorine. As a result, we tried a wet chemical technique involving impinges with analysis by ion chromatography. However, repeated attempts to use this technique also failed to yield meaningful results. For example, data using this technique revealed chlorine concentrations as high as four times the expected amount for some of the samples.

The failure of the impinger technique led us to resort to the use of Dräger tubes for chlorine analysis. Dräger tubes specific to chlorine and HCl were used for this purpose. The Dräger tubes were placed at the reactor exit and the time required for the color change was observed. The Dräger tube analysis is believed to be within ± 30 percent.

Dräger tube results for the CK-302 catalyst are summarized in Table 15. Both HCl and Cl_2 were observed in the effluent stream. However, in all cases, the amount of Cl_2 was less than 5 percent of the total expected chlorine content. The total chlorine atoms in HCl and Cl_2 are up to 55 percent less than the theoretically expected chlorine atoms. This is not surprising because the accuracy of the Dräger tube analysis is believed to be within ± 30 percent.

TABLE 15. CHLORINE BALANCE FOR CHLORINATED STREAM OXIDATION
OVER CK-302 CATALYST

Time on stream (days)	HCl (ppm)	Cl_2 (ppm)	Total chlorine atoms	Expected chlorine atoms*
90	635	14	663	1088
150	446	11	468	1088
180	564	18	600	1068
210	689	27	743	1088

* Calculated based on the chlorocarbons in the feed.

Chlorine can be present in the effluent stream in the form of HCl, Cl_2, chlorinated hydrocarbons, or chlorine-oxygen compounds. It is unlikely that any chlorine-oxygen compound would be stable under the reaction conditions. Also, since the carbon balance is better than ± 5 percent, any chlorine in the effluent stream should be present in the form of HCl or Cl_2. The results from Dräger tube analysis suggest that either the chlorine is retained by the catalyst/reactor or there is a significant error involved with this technique. The latter seems to be more likely because retention of any significant amount of chlorine on the catalyst would result in loss of catalyst activity which was not observed over this catalyst.

28

b. Mixed Stream

Table A-4 in Appendix A summarizes the activity data for the oxidation of mixed stream over CK-302 catalyst. The catalyst did not lose any activity when used for 129 days on stream. The total conversion was above 99 percent at 350 °C. This is in contrast to the chlorinated stream oxidation where a temperature of 400 °C was required to achieve > 99 percent conversion. Significant quantities (3 to 6 ppm) of 1,1,2-trichloroethane were formed over this catalyst, as shown in Figure 6. Some trace amounts of chloroform were also formed over this catalyst. The formation of 1,1,2-trichloroethane appears to be characteristic of the CK-302 catalyst as also observed during chlorinated stream oxidation.

Table 16 summarizes the chlorine balance over this catalyst. Both HCl and Cl_2 were formed with the Cl_2 concentration being less than 1 percent of the total theoretical chlorine present in the effluent stream. The total chlorine atoms measured by this technique were much lower than the expected amount (156 ppm). Again, this is attributed to the error in the analytical technique.

4. ARI Catalyst

The ARI catalyst was used for the oxidation of chlorinated and mixed-stream oxidation for long-term deactivation runs. The mixed-stream oxidation was studied in both the fixed-bed and fluid-bed reactor. The chlorinated-stream oxidation was studied only in fixed-bed reactor.
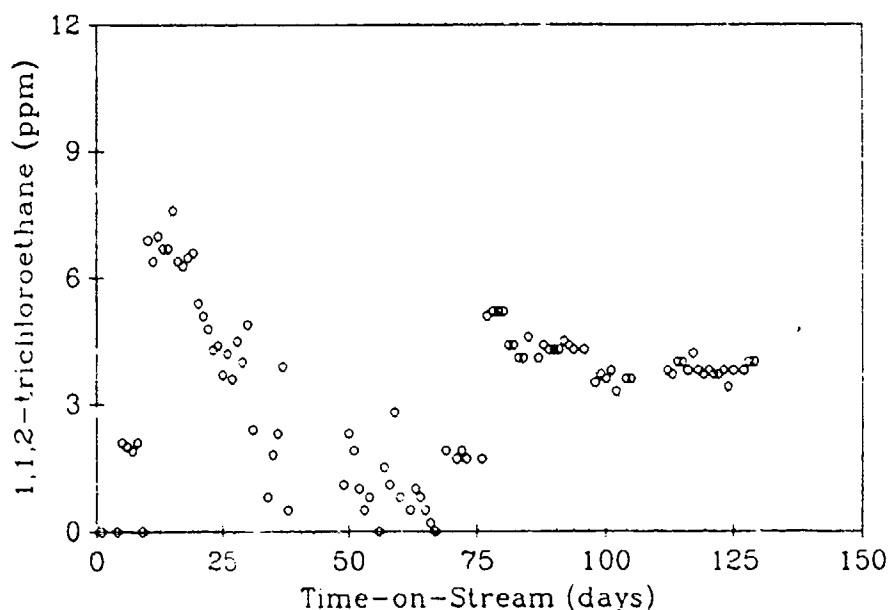
Figure 6. Concentration of 1,1,2-Trichloroethane in the Effluent Stream for Mixed-Stream Oxidation Over CK-302 Catalyst

TABLE 16. CHLORINE BALANCE FOR MIXED-STREAM OXIDATION OVER CK-302 CATALYST

Time on stream (days)	HCl (ppm)	Cl₂ (ppm)	Chloroform and 1,1,2-trichloro-ethane	Total chlorine atoms	Expected chlorine atoms*
30	68	1.3	4.9	85.3	156
60	38	1.7	0.8	43.8	156

* Calculated based on the chlorocarbon in the feed.

a. Fluid-Bed Reactor

The deactivation of the chromia-alumina catalyst for the oxidation of chlorinated (B) and mixed (C) streams was studied in the two fluid-bed reactors under similar hydrodynamic conditions. The gas flow was just sufficient to keep the bed agitated at the reaction temperature (visually verified) and thus the hydrodynamic regime of these reactors corresponded to conditions of incipient fluidization. The initial temperature (360 °C for the oxidation of Stream B and 385 °C for the oxidation of Stream C) was such that the total conversion was above 99 percent. Conversion was maintained at this level by increa sing the temperature as needed.

The catalyst used for the oxidation of Stream B lost very little activity even after 238 days on stream as can be seen from Table , . 5 in Appendix A. The conversions of 1,1-dichloroethylene, 1,2-dichloroethane, and trichloroethylene were greater than 99 percent, but the conversion of methylene chloride was only 97 to 98 percent as seen from Figure 7. In addition to the unconverted feed compounds, the effluent stream contained partially oxidized products (<1 ppm) such as chloroform and 1,1,2-trichloroethane, and total oxidation products such as HCl and Cl₂. The amount of Cl₂ in the effluent stream was less than 5 percent of the total chlorine in the feed. Table 17 summarizes the chlorine balance as a function of time on stream. Both carbon monoxide and carbon dioxide were formed over this catalyst. The proportion of CO (23 percent of the total CO$_x$) was constant with time on stream as shown in Figure 8.

The oxidation of Stream C using a fresh sample of the same chromia-alumina catalyst required a higher initial temperature (385 °C) to achieve >99 percent total conversion. The catalyst also exhibited a steady deactivation, requiring an increase in the operating temperature from 385 °C to 418 °C over 210 days on stream to maintain the total conversion level above 99 percent. The activity data are summarized in Table A-6. The temperature increase to maintain a constant conversion for Stream C oxidation is summarized in Figure 9. The catalyst lost activity primarily for the oxidation of benzene and
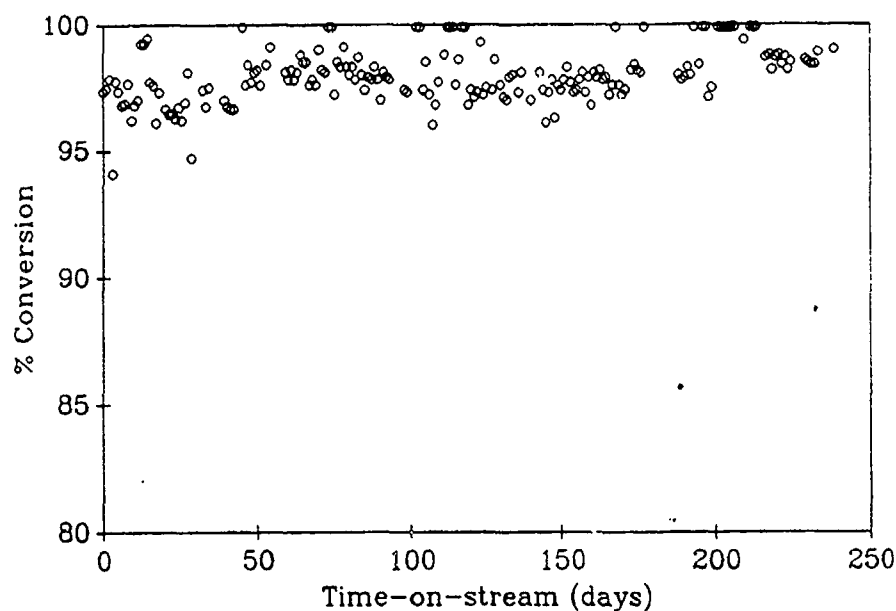
Figure 7. Conversion of Methylene Chloride Over ARI Catalyst Used for the Oxidation of Chlorinated Stream in the Fluid-Bed Reactor

TABLE 17. CHLORINE BALANCE FOR CHLORINATED STREAM OXIDATION OVER ARI CATALYST IN FLUID-BED REACTOR

Time on stream (days)	HCl (ppm)	Cl₂ (ppm)	Total chlorine atoms	Expected chlorine atoms*
117	613	13.4	639.8	1088
153	735	19	773	1088
165	879	22	923	1088
214	1041.7	22.6	1086.8	1088

* Calculated based on the chlorocarbons in the feed.

trichloroethylene; however, the activity for other compounds remained high (above 99 percent). The conversion of benzene was only 85 to 90 percent and trichloroethylene was 95 to 97 percent. This is shown in Figure 10. The proportion of CO was 11 to 13 percent of the total CO_x and remained constant with time on stream as for Stream B, as seen in Figure 11. Although the number of catalytic sites decreased with time as evidenced by the decrease in catalytic activity, the constant CO selectivity suggests that of Chlorinated Stream in Fluid Bed Reactor the chemical nature of the remaining sites was unaffected.

Both Cl_2 and HCl were formed; however, the amount of Cl_2 was small. Also, no Cl_2 was detected at 59 days on stream. The concentration of Cl_2 slowly increased to 0.2 ppm. Table 18 summarizes the chlorine balance for C Stream oxidation.

31
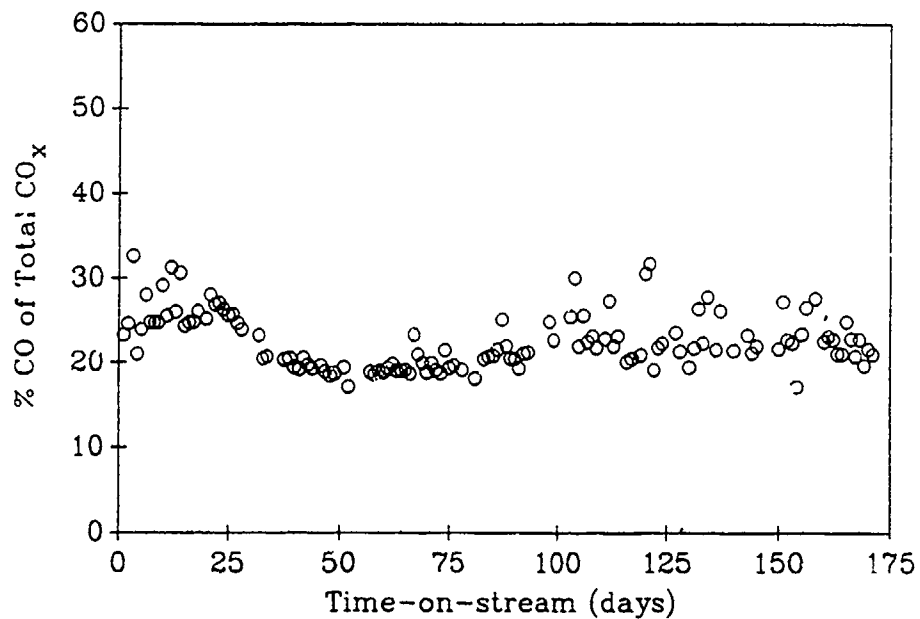
Figure 8. The Concentration of CO (Percent of Total CO_x) Over the ARI Catalyst for Chlorinated Stream Oxidation in Fluid-bed Reactor
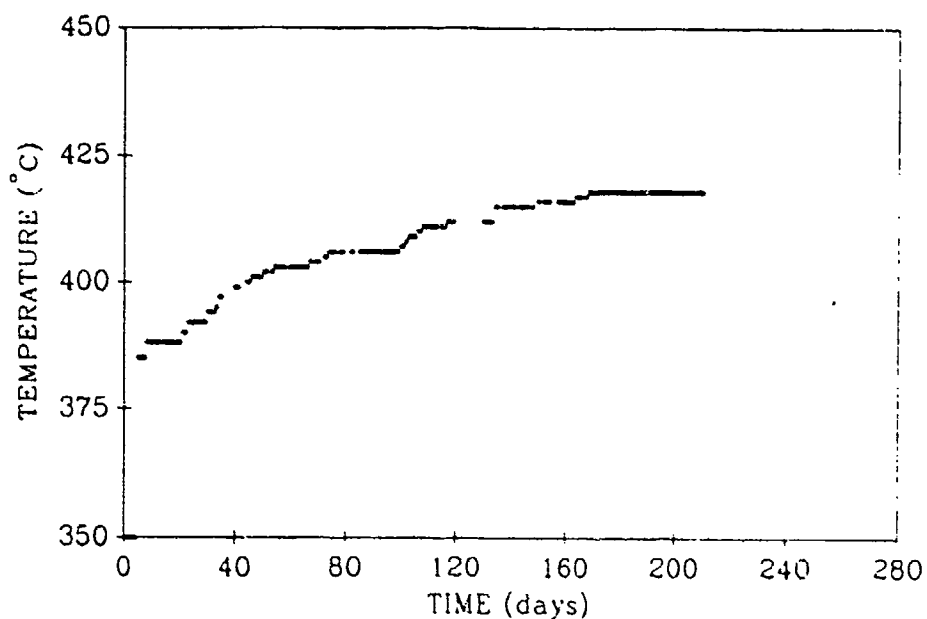
Figure 9. Temperature Required to Maintain Total Conversion Above 99 Percent for Mixed-stream Oxidation Over ARI Catalyst in Fluid-bed Reactor
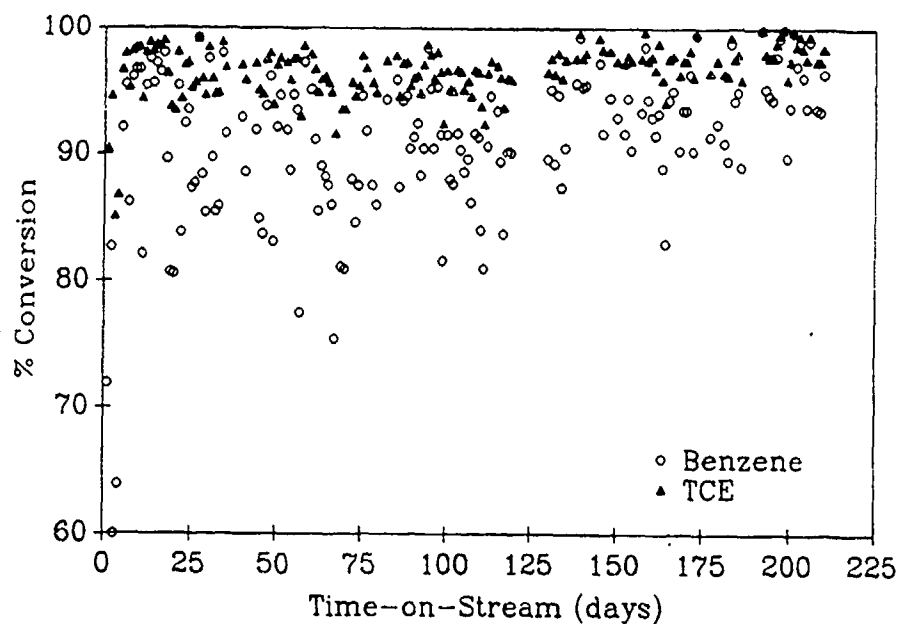
Figure 10. Conversion of Benzene and Trichloroethylene Over ARI Catalyst Used for the Oxidation of Mixed-stream in Fluid-bed Reactor
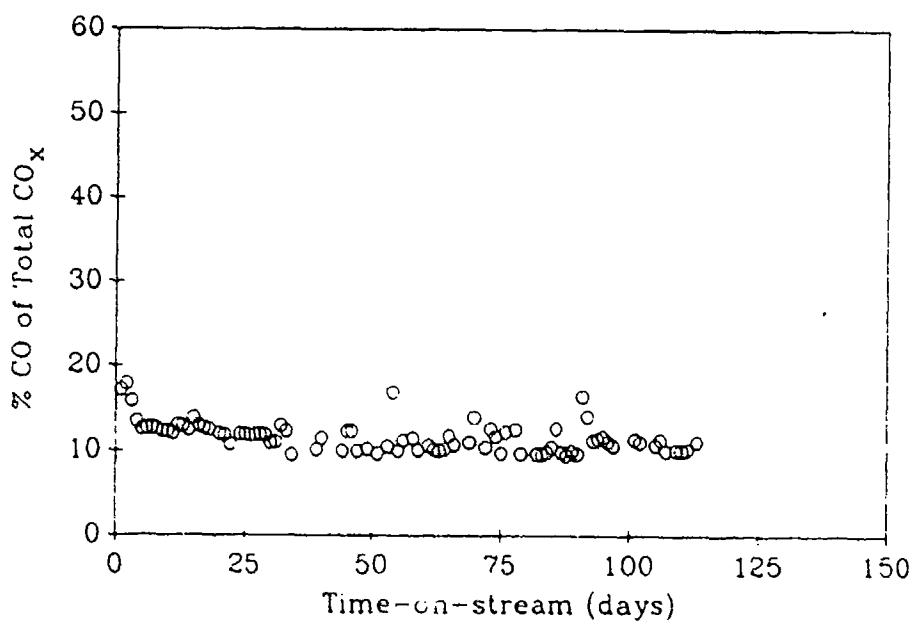
Figure 11. The Concentration of CO (Percent of Total Co_x) Over the ARI Catalyst for Mixed-stream Oxidation in Fluid-bed Reactor

33

TABLE 18. CHLORINE BALANCE FOR MIXED STREAM OXIDATION OVER ARI CATALYST IN FLUID-BED REACTOR

Time on stream (days)	HCl (ppm)	Cl_2 (ppm)	Total chlorine atoms	Expected chlorine atoms[a]
59	79.9	N.D.	79.9	156
95	60	0.06	60.1	156
107	78.7	0.2	79.2	156
156	72.2	0.2	72.6	156

[a] Based on the chlorocarbon in the feed.
N.D. = Not detectable.

Coke formation, though not directly observed, cannot be ruled out as a mechanism of deactivation in the oxidation of Stream C on this catalyst. Although the carbon balance was within ±5 percent for both Streams B and C, the retention of even a small amount of coke on the catalyst surface can cause pore plugging in the long run and hence a loss in activity. For example, Ramanathan and Spivey (Reference 15) observed that an air stream passed over this same chromia-alumina catalyst after being used for the oxidation of 1,1-dichloroethylene under similar reaction conditions contained carbon dioxide, probably formed by the oxidation of carbon on the catalyst surface.

The used catalysts were characterized by BET, elemental analysis, and XPS. Table 19 compares the BET surface area of used ARI catalysts with the fresh catalyst. The catalyst used for the oxidation of B Stream did not lose any surface area. However, the surface area of the catalyst used for C Stream oxidation decreased to 151 m^2/g. This catalyst also deactivated corresponding to a temperature increase of 33 °C suggesting that deactivation may be related to the decrease in surface area which probably was caused by sintering.

The binding energies of O 1s and Cr 2p are summarized in Table 20. The Cr $2p_{1/2}$ binding energy in the fresh catalyst was 586.3 eV and the 2p separation energy was 9.8 eV suggesting that Cr is in the form of Cr_2O_3 on the catalyst surface. The Cr 2p and O 1s binding energies in the used catalyst were similar to that in the fresh catalyst.

XPS analysis of the ARI catalysts showed the Cl 2p binding energy peak in both the used and fresh catalysts. Since the chlorine amount was small, quantitative calculations could not be performed. Thus, these results do not provide any evidence of chlorine retention on the catalyst surface.

The chromium content in the bulk fresh and used ARI catalysts was analyzed and the results are summarized in Table 21. There was no change in the chromium content of

34

TABLE 19. BET SURFACE AREA OF ARI CATALYST

Catalyst	BET m^2/g
Fresh	188
Fluid - chlorinated	187
Fluid - mixed	151

TABLE 20. XPS RESULTS OVER ARI CATALYSTS

Catalyst	Binding Energy, eV			Separation energy
	O 1s	Cr $2p_{1/2}$	Cr $2p_{3/2}$	Cr 2p
Fresh	530.2	586.3	576.5	9.8
Used for Chlorinated	530.5	586.2	576.7	9.5
Mixed	530.0	586.2	576.3	9.9

TABLE 21. CHROMIUM CONTENT IN ARI CATALYSTS

Catalysts	Bulk chromium content, %
Fresh	9.2
Used for Chlorinated stream	8.3
Mixed stream	9.3

the ARI catalyst used for mixed stream oxidation. However, the catalyst used for chlorinated stream oxidation contained 10 percent less chromium after reaction compared to the fresh catalyst. The loss in chromium may be related to the formation of volatile chromium oxychloride which vaporizes from the catalyst. It is interesting to note that in spite of the chromium loss, the overall activity of the catalyst used for the oxidation of chlorinated stream did not change significantly.

The catalyst used for mixed-stream oxidation did not lose any chromium; however, it suffered some deactivation. This would suggest that the loss in activity is not related to the chromium content of the catalyst. However, a physical deactivation mechanism such as sintering (as seen by the decrease in BET surface area) or coking may be responsible for the loss in catalyst activity for the oxidation of mixed stream.

b. Fixed-bed Reactor

The effect of reactor configuration was studied by conducting the oxidation of Stream B in a fixed-bed reactor and comparing the results to those in the fluid-bed reactor. An initial temperature of 350 °C was needed to achieve >99 percent total conversion. The activity data are summarized in Table A-7 in Appendix A. As in the case of the fluid-bed reactor, the catalyst did not show any overall change in the activity with time on stream. However, the proportion of CO was higher than in the fluid-bed reactor, probably because of reduced backmixing in a fixed-bed reactor. Furthermore, the amount of CO increased from 32 percent (of the total CO_x) at the start of the run to 54 percent after 150 days on stream. This is represented in Figure 12. The increase in the proportion of CO in the effluent stream suggests a decline in the oxidation activity of the catalyst, although the overall
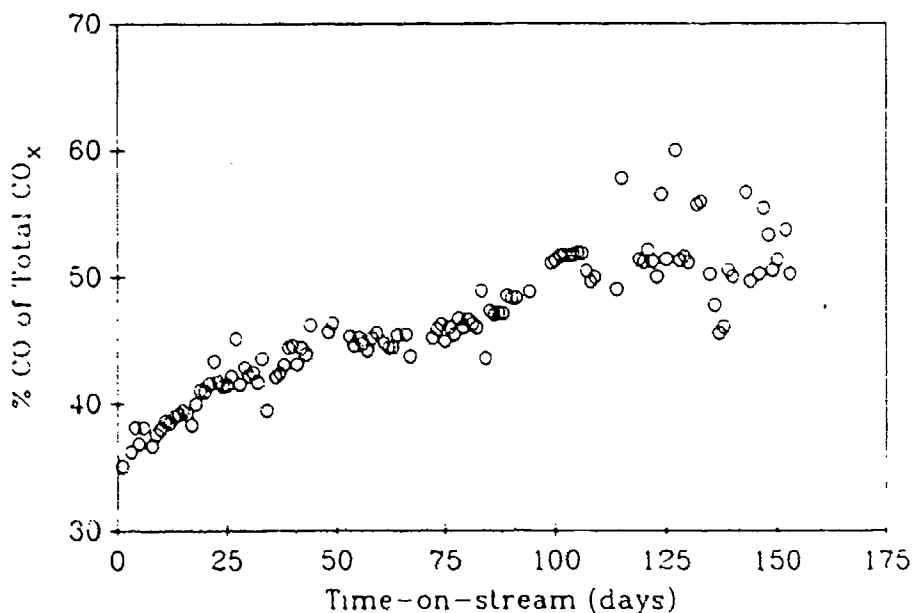
Figure 12. The Concentration of CO (Percent of Total CO_x) Over the ARI Catalyst for Chlorinated Stream Oxidation in Fixed-bed Reactor

36

total conversion did not change. A similar increase in the proportion of CO in the effluent stream was observed by Young (Reference 16) in the oxidation of methylene chloride over a commercial 12.5 weight percent chromia/alumina catalyst. The amount of Cl_2 in the fixed-bed reactor was lower than in the fluid-bed reactor. The chlorine balance is summarized in Table 22.

TABLE 22. CHLORINE BALANCE FOR CHLORINATED STREAM OXIDATION OVER ARI CATALYST IN FIXED-BED REACTOR

Time on stream (days)	HCl (ppm)	Cl_2 (ppm)	Total chlorine atoms	Expected chlorine atoms[a]
125	794	7	808	1088
150	335	5	345	1088

[a] Calculated based on chlorocarbons in the feed.

The deactivation runs on the fixed-bed reactor were terminated after 153 days on stream by cooling the catalyst in an inert gas. A visual observation of the catalyst revealed a distinct color change from brown to green in the upstream third of the bed. The next third of the bed was greenish brown, while the remaining third of bed had the original brown color. This is shown in Figure 13. Analysis of the surface of the three catalyst sections by XPS did not reveal any change in the Cr 2p binding energy from the outlet of the bed to the inlet as shown in Table 23. Although we have no direct evidence correlating the catalytic activity and selectivity with the catalyst properties, the increase in the CO/CO_2 ratio and the observed color change suggest that the first third of the bed had lost its catalytic selectivity. It can be concluded that as the front portion of the bed deactivates, the reaction zone moves progressively down the bed until the bed exit is reached. Thus, although part of the catalyst has apparently deactivated, the overall conversion would not change until the reaction zone reached the bed exit, at which point the total conversion would rapidly decrease. Of course, such a color change was not observed in the fluid-bed reactor because of the constant motion of the catalyst particles in the reactor.

5. Feed Stream/Reactor/Catalyst Type Comparison

a. Differences in "Mixed-Stream" and Chlorinated VOC Oxidation

Oxidation reactions of both "mixed stream" and chlorinated stream were studied using the ARI catalyst and the same hydrodynamic conditions in fluid-bed reactors. Certain differences that were observed in the two sets of data follow:

• The temperature required for >99 percent conversion of mixed stream was higher than that for chlorinated-stream oxidation.
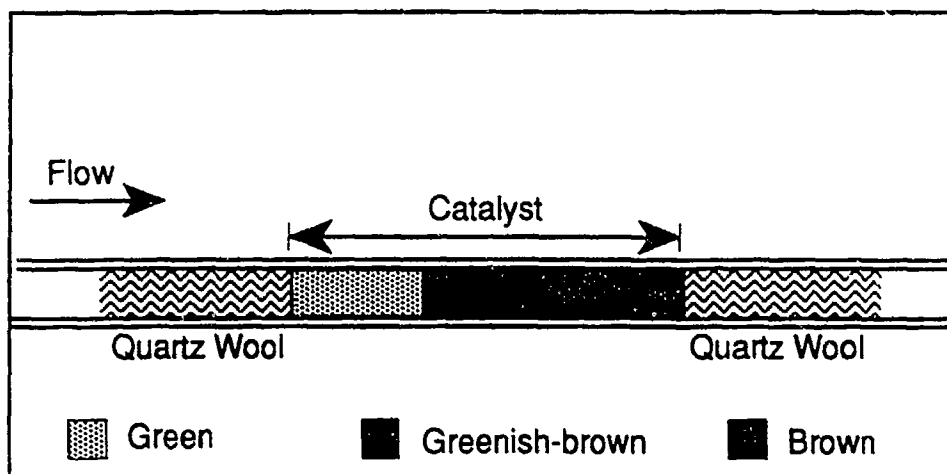
Figure 13. Schematic of ARI Catalyst Used for 153 Days for the Oxidation of Chlorinated Stream In Fixed-bed Reactor

TABLE 23. COMPARISON OF BINDING ENERGIES BETWEEN FRESH AND USED ARI CATALYST FOR CHLORINATED STREAM OXIDATION IN FIXED-BED REACTOR

Catalyst/section	Binding energy, eV			Separation eV energy
	Al 2p	Cr 2p$_{1/2}$	Cr 2p$_{3/2}$	Cr 2p
Unused	73.6	586.3	576.5	9.8
Bottom section	74	586.4	576.4	10
Middle section	74.4	586.4	576.6	9.8
Top section (front)	74.4	586.4	576.8	9.6

- The catalyst for mixed-stream oxidation exhibited some deactivation and the temperature was increased to 418 °C to maintain total conversion level above 99 percent.

- The concentration of CO in the effluent of mixed stream oxidation was low (11 to 13 percent of the total CO_x) compared to that in the effluent of chlorinated stream oxidation (20 to 25 percent of the total CO_x).

b. Differences Between Fixed-bed and Fluid-bed Reactors (ARI Catalyst)

Some of the differences between the fixed-bed and fluid-bed operation for the oxidation of chlorinated stream using the ARI catalyst are summarized below:

- The amount of CO formed in the fixed-bed reactor was greater than in the fluid-bed reactor. The CO concentration increased from 32 percent (of the total oxidation products) to 54 percent during 153 days on stream operation. The percent of CO (of the total oxidation products) in the effluent stream of the fluid-bed reactor was constant (25 percent).

- The amount of chlorine produced in the fluid-bed reactor was greater than that in the fixed-bed reactor.

- The color of catalyst in the fixed-bed reactor changed from brown to greenish brown. No such color change was observed in the fluid-bed reactor.

c. CK-302 and ARI Catalyst Differences for Mixed-Stream Oxidation

Some differences in the activity and selectivity for the mixed-stream oxidation that were observed over these two catalysts are:

- The ARI catalyst lost some activity and the temperature was increased to 418 °C from 385 °C for 99 percent conversion. The CK-302 catalyst exhibited 99 percent conversion at 400 °C. Furthermore, no decrease in activity was observed, even after 3,000 hours on stream. (Note the high space velocity for ARI catalyst, 12000 h⁻¹, compared to the CK-302 catalyst, 3700 h⁻¹.)

- The only partial oxidation product observed over ARI catalyst was 1,1,2-trichloroethane (< 0.6 ppm). The effluent stream from the CK-302 catalyst had both 1,1,2-trichloroethane and trace quantities of chloroform. The amount of 1,1,2-trichloroethane was significantly higher (4 to 6 ppm) over the CK-302 catalyst.

- Both CO and CO_2 were formed over the ARI catalyst; however, only CO_2 was observed over the CK-302 catalyst.

d. Comparison of Fresh and Used Catalyst Characteristics

Some differences in catalyst characteristics between the used and fresh catalyst were observed. These are summarized in Table 24. Since the CK-302 did not show any deactivation, the used catalyst was not characterized.

TABLE 24. COMPARISON OF FRESH AND USED
CATALYST CHARACTERISTICS

Catalyst/property	Fresh	Used
1. Pt/Ni BET, m^2/g Appearance	248 -	Decreased by 10% Black spots on the catalyst surface
2. Carus XPS data	Single peak in the O 1s binding energy region	Wide peak (deconvoluted into 3 peaks) in the O 1s binding energy region. This suggests a change in the state of manganese oxide species.
3. ARI a. Fixed-bed-chlorinated stream BET, m^2/g Chromium content, % Appearance	 188 9.2 -	 Decreased by 6% Decreased by 10% Color changed from brown to green of top third of the bed
CO selectivity, %	32	54
b. Fluid-bed-chlorinated BET, m^2/g Chromium content, %	 188 9.2	 No change Decreased by 10%
c. Fluid-bed-mixed stream BET, m^2/g Chromium content, %	 188 9.2	 Decreased by 20% No change

40

SECTION V

DEACTIVATION MODELING

Of the four catalysts investigated in this work, only the Carus catalyst exhibited significant deactivation. This catalyst required a temperature increase of 85 °C over 297 days for the oxidation of hydrocarbon stream. Because the other catalysts did not require any appreciable temperature increase, the deactivation model was developed only for the Carus catalyst.

A. DEACTIVATION MODEL FOR CARUS CATALYST

The catalyst deactivation was studied at constant conversion of >99 percent. The temperature was increased periodically to compensate for the loss of intrinsic catalytic activity. A plot of the temperature required to maintain a constant conversion as a function of time on stream was shown in Figure 6. The overall temperature increase was 85 °C over 297 days on stream (7,128 hours). A simple model was developed to fit these experimental data and to predict the total catalyst time.

Assuming that the deactivation rate is a function of activity alone,

$$- r_d = - \frac{dS}{dt} = k_d S^n \qquad (9)$$

where

$$
\begin{aligned}
r_d &= \text{rate of deactivation} \\
S &= \text{activity term} \\
n &= \text{order of deactivation reaction} \\
k_d &= \text{rate constant of deactivation} \\
&= A_d \exp(-E_d/RT) \\
E_d &= \text{activation energy for the deactivation reaction.}
\end{aligned}
$$

Since the conversion is constant, the rate constant of the oxidation reaction can be expressed as

$$k = \frac{1}{S} k_o = A \exp(-E_A/RT) \qquad (10)$$

where k is the rate constant of the main reaction, R is the gas constant, A is the preexponential factor for the main reaction (oxidation of VOC), T is the catalyst temperature, E_A is the activation energy of the main reaction, k_o is the rate constant at $t = 0$, $T = T_o$. E is the activation energy for the main reaction.

41

From Equation (10)

$$A \exp(-E_A/RT) = \frac{1}{S} \exp(-E_A/RT_o)$$

rearranging,

$$1/T = R/E_A \ln S + \frac{1}{T_o} \tag{11}$$

assuming, first order deactivation kinetics, i.e., $n = 1$ in Equation (9)

$$-\frac{dS}{dt} = A_d \exp(-E_d/RT) \, S \tag{12}$$

substituting Equation (11) in (12)

$$-\frac{dS}{dt} = A_d \exp(-E_d/RT_o) \, S^{\left(1 - \frac{E_d}{E_A}\right)} \tag{13}$$

Integration of Equation (13) gives

$$t = \frac{E_A}{E_d \, A_d} \exp(E_d/R \, T_o) \left[1 - S^{E_d / E_A}\right] \tag{14}$$

substituting for S in Equation (14) yields the comparison for time on stream as a function of reaction temperature.

$$t = D \left[1 - \exp\left[B\left(\frac{1}{T} - \frac{1}{T_o}\right)\right]\right] \tag{15}$$

$$\text{where} \quad D = \frac{E_A}{E_d A_d} \exp\left(\frac{E_d}{R \, T_o}\right) \quad \text{and} \tag{16}$$

$$B = -\frac{E_d}{R} \tag{17}$$

By least-square fit of the experimental data (Table A-2) to Equation (15), we get

D = 296.1 days
3 = 15961.9 k

Since B   = - E_d/R

E_d = 31.5 kcal/gmol.

The experimental data are compared with the calculated values using Equation (15) in Figure 14. The model represents a fairly good fit after 160 days on stream, that is, when the catalyst starts deactivating. At high temperature (> 380 °C), the model underpredicts the time on stream.

Because the maximum operating temperature recommended for this catalyst is 500 °C, Equation (15) can be used to predict the life of the catalyst

$$t_{life} = 296 \text{ days.}$$

However, as mentioned above, the model underpredicts the observed catalyst lifetime.

If Equation (15) is modified by adding a third parameter, C

$$t = D\left[1 - \exp\left\{B\left(\frac{1}{T} - \frac{1}{T_o}\right)\right\}\right] + C. \tag{18}$$

Least-square fit to Equation (18) gives

D   = 299.3 days
B   = 4770.4 K
C   = 106 days.

The time-temperature relationship predicted by Equation (18) is compared with the experimental data in Figure 15. Because of the third parameter, C, the predicted time-temperature curve starts after C (106) days on stream. After that time, the predicted time-temperature relationship compares very well with the experimental data. The modified model predicts the catalyst lifetime of 362 days, which more closely corresponds to the life that would be expected from the experimental results. The third parameter C has the units of time. C is believed to be related to the breakthrough of the deactivation wave, after which the decrease in conversion with time on stream becomes observable at bed exit. Figure 15 shows this time to be 150 days. This is comparable with the value of C (106 days).

The parameter B can be used to determine the activation energy of the deactivation reaction (E_d). Equation (17) predicts this value to be 31.7 kcal/mol for the model given by Equation (15). The apparent activation energy for the main reaction over the hopcalite could not be measured because of the deactivation of this catalyst below 300 °C. However, if we assume that the apparent activation energy for the main reaction over the hopcalite catalyst is similar to that over the Pt/Ni catalyst which is 25 kcal/mol, the activation energy for the deactivation reaction over the hopcalite predicted by Equation
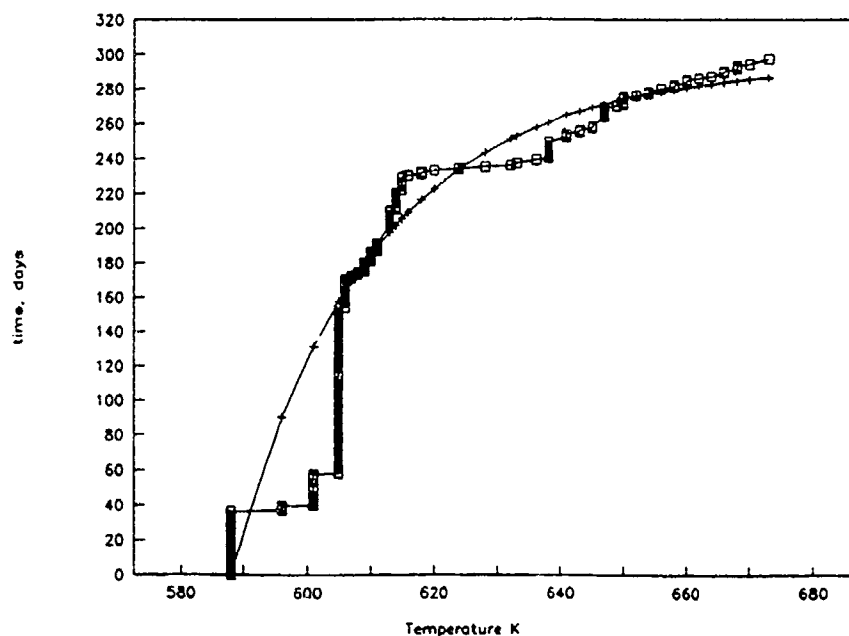
Figure 14. Comparison of the Experimental Data Over Carulite Catalyst with that Predicted by the Model.
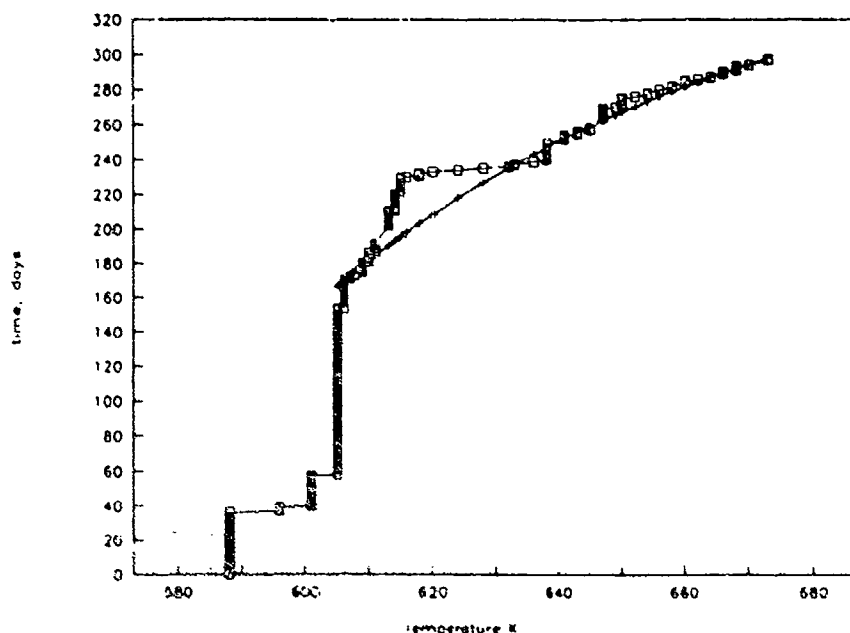
Figure 15. Comparison of the Experimental Data Over Carulite Catalyst with that Predicted by the Modified Model

44

(17) is higher than the apparent activation energy for the main reaction. This suggests that the control variable, that is, temperature, that is used to control the effects of deactivation actually preferentially promotes the deactivation process. This represents an unstable process which was not observed in our experiment. The modified model, Equation (18), predicts a more reasonable value of 9.5 kcal/mol for E_d over the hopcalite catalyst. This value being lower than the apparent activation energy for the main reaction, any increase in temperature would preferentially promote the main reaction as observed by our experimental results.

SECTION VI

ECONOMIC ANALYSIS

The deactivation of these catalysts increases the annual operating costs for the incinerator for two primary reasons. First, as the catalyst begins to deactivate, the temperature must be raised to maintain constant conversion. This requires extra fuel for the preheater. Second, after the catalyst has completely deactivated, it must be replaced. This cost must be accounted for over the operating life of the catalyst.

In evaluating the costs of deactivation, the following assumptions are made:

- Constant conversion operation. This is typical of the way field units are designed to operate to achieve constant emission reduction. The experiments described herein were carried out at >99 percent conversion.

- 50% energy recovery. This would be typical of the energy recovery expected from a primary heat exchanger on a field unit.

- 2,000 scfm catalytic oxidation unit size. This corresponds to a water feed to the air stripper of 357 gpm (at a G/L ratio of 42 [Reference 7]). Though this is larger than most field units, capital costs are not readily available nor directly comparable among vendors for much smaller systems.

- All direct and indirect equipment, installation, and annualized costs for the catalytic oxidation unit are those given by EPA (Reference 11, p. 3-52).

Because the unit size is the same for all catalysts considered, the capital cost differs only in that a more expensive fluid bed is required for the ARI catalyst. Annual operating costs (labor, maintenance, etc.) are assumed to be the same for all catalysts with the exception of:

- Auxiliary fuel costs (natural gas is assumed to be the fuel). This is the largest single operating cost for all systems. Deactivation causes more fuel to be used to maintain constant conversion with time.

- Electricity costs. The primary electrical costs are for the fan used for air flow through the unit. Because the pressure drop is generally higher for a fluid bed than a fixed-bed unit (Reference 11), the electrical costs are somewhat higher for the ARI catalyst than for the other three.

- Catalyst replacement costs. Each catalyst must be periodically replaced. For the Carus catalyst, the lifetime can be estimated from the experimental results presented herein, even though it did not completely deactivate. For the other catalysts, the lifetime cannot be estimated.

46

The economic analysis is carried out by evaluating each of these three costs and as functions of the experimentally observed deactivation. These costs are then summarized, along with other operating costs, to calculate the total annualized costs.

A. AUXILIARY FUEL COSTS

The usage rate of natural gas auxiliary fuel for the catalytic incinerator shown schematically in Figure 16 is given by the following equation, adapted from EPA (Reference 11, p. 3-40), and is based on an energy balance around the incinerator:

$$Q_{af} = \frac{\rho_{wo}Q_{wo}[C_{pm_{air}}\{1.1(T_{ri}-\frac{\Delta h_{cwo}}{C_{pm_{air}}})-0.5(T_{ri} - \frac{\Delta h_{c_{wo}}}{C_{pm_{air}}} + T_{wi})-0.1T_{ref}\} + \Delta h_{c_{wo}}]}{\rho_{af}[-\Delta h_{c_{af}} - 1.1\ C_{pm_{air}}(T_{ri} - \frac{\Delta h_{c_{wo}}}{C_{pm_{air}}} - T_{ref})]} \tag{20}$$

where Q_{af} = flow rate of natural gas auxiliary fuel to the unit preheater, scfm

ρ_{wo} = density of the inlet waste gas, 0.0739 lb/scf at 77 °F, 1 atm

Q_{wo} = flow rate of waste gas from the air stripper through the preheater, 10,000 scfm for this example

$C_{pm_{air}}$ = mean heat capacity of air over the range of operation of the incinerator, 0.255 Btu/lb °F

T_{ri} = inlet temperature to the catalyst combustion chamber, °F

$\Delta h_{c_{wo}}$ = heat of combustion of the waste gas, Btu/lb

T_{wi} = inlet temperature of the waste gas from the air stripper to the catalytic oxidation unit, chosen to be 77 °F in this example

T_{ref} = reference temperature, 77 °F

ρ_{af} = density of natural gas, calculated as methane, 0.0408 lb/ft³ at 77 °F

Δh_{caf} = heat of combustion of the natural gas auxiliary fuel, 21,502 Btu/lb
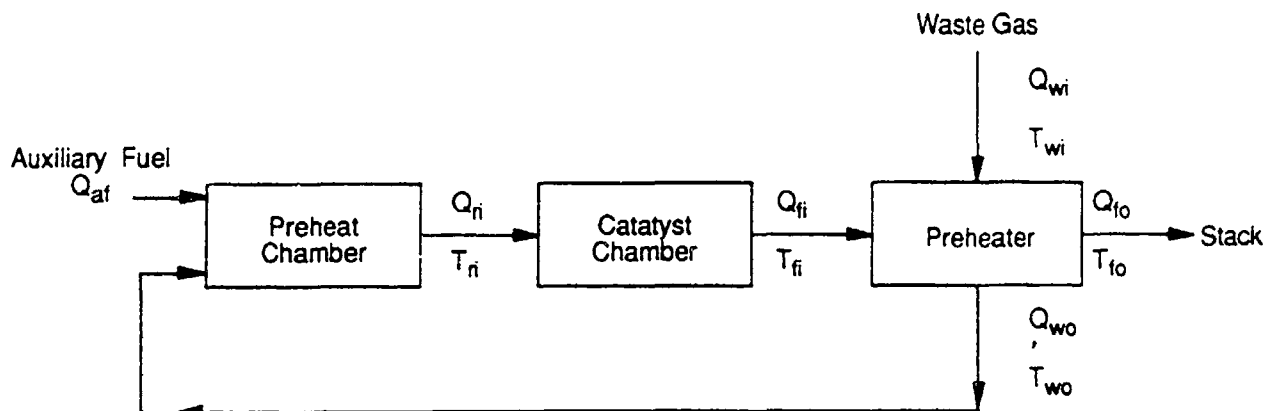
Figure 16. Schematic of Catalytic Incinerator

The assumptions leading to this expression include the following:

*   The organic content of the waste gas stream is low enough so that no auxiliary air is needed to provide combustion air for the auxiliary fuel in the preheater section.

*   Energy loss from the unit to the atmosphere through the walls of the unit (not the flue gas) is 10 percent of the total energy input.
*   Heat capacities of the waste gas are independent of composition. This is true for dilute waste gases of the type considered here.

*   The mean heat capacities above the reference temperature are independent of temperature.

All values in this equation are known except T_{ri}, the inlet temperature to the catalyst bed. This value increases gradually over time as the catalyst deactivates and thus the auxiliary fuel requirement increases. T_{ri} thus corresponds to the inlet temperature to the catalyst bed that is needed to maintain constant conversion.

Equation (20) above gives the **instantaneous** auxiliary fuel usage rate in ft^3/min as a function of the inlet temperature to the catalyst bed, T_{ri}. The mathematical link between this expression and the experimental deactivation results is the deactivation model, which expresses T_{ri} as a function of time, t.

48

This time-temperature deactivation function can be expressed as shown in Equation (21)

$$t = D\left[1-\exp\left(B(\frac{1}{T_{ri}}-\frac{1}{T_o})\right)\right]+C \qquad (21)$$

where T_o is the initial temperature needed to maintain > 99 percent conversion.

The **total** auxiliary fuel usage rate over the life of the catalyst is then the integral of Equation (20) from t=o to t=t_{life}, where t_{life} is the lifetime of the catalyst, i.e., the time before T_{ri} reaches the maximum temperature allowed by the vendor. Equation (21) can be rearranged to solve explicity for T_{ri} and then substituted into Equation (20). An expression of the following form is obtained:

$$Q_{af} = \frac{aT_{ri}+b}{cT_{ri}+d} \qquad (22)$$

In Equation (22) constants a,b,c, and d are defined only by the **properties of the gases** and the **system size** (i.e., total volumetric flow rate). They do **not** depend on the deactivation of the catalyst. Equation (22) becomes a time-dependent function, Q_{af} (t), by substituting Equation (21) into Equation (22), yielding an expression of the form

$$Q_{af}(t) = \frac{[aBT_o + bB] + bT_o \ln[1-\frac{t-C}{D}]}{[cBT_o + dB] + dT_o \ln[1-\frac{t-C}{D}]} \qquad (23)$$

where B, C, and D depend **only** on the experimental deactivation results and are defined by the deactivation model given in Equation (21). The **total** amount of auxiliary fuel used over the lifetime of the catalyst is thus:

$$\int_o^{t_{life}} Q_{af}(t)dt = \int_o^{t_{life}} \frac{[aBT_o + bB] + bT_o \ln[1-\frac{t-C}{D}]}{[cBT_o + dB] + dT_o \ln[1-\frac{t-C}{D}]} dt \qquad (24)$$

For the Carus catalyst, which is the only catalyst to show substantial deactivation over the time scale of the experiments,

B = 8586 °F
C = 1.526 x 10^5 min
D = 4.310 x 10^5 min.

49

For the hydrocarbon gas tested on the Carus catalyst and for a 2,000 scfm system the values of a, b, c, and d are given by:

$$a = +2.26 \times 10^{+1} \quad \text{Btu/min - }°F$$
$$b = -5.04 \times 10^{-3} \quad \text{Btu/min}$$
$$c = -1.144 \times 10^{-2} \quad \text{Btu/ft}^3 \text{ -}°F$$
$$d = +8.757 \times 10^{2} \quad \text{Btu/ft}^3$$

From the model given in Equation (21) the catalyst lifetime, t_{life} is 5.213 x 10^5 minutes (362 days), that is, the model predicts it will take t_{life} minutes before T_{ri} reaches 500 °C, the maximum temperature recommended by the vendor. Substituting this value of t_{life} and the above parameters into Equation (24) and integrating, the **total** volume of natural gas used over the 362-day life of the catalyst is:

$$Q_{af}^{tot} = 5.75 \times 10^{6} \ ft^3 \ .$$

This value is then used to calculate the annual usage of natural gas (in ft^3). Because the catalyst life is essentially 1 year (allowing, for example, 3 days for shutdown to reload new catalyst), Q_{af}^{tot} and the **annual** usage of natural gas are numerically equal. This would not generally be true. In other cases, the annual usage rate would, of course, be calculated for each 365-day period following startup. The annual usage of natural gas may vary from year to year; nevertheless, the methodology above would be used to calculate Q_{af}^{tot} over the catalyst life.

B. ELECTRICAL COSTS

Electrical costs are almost exclusively due to the electric power used by the fan needed to move the waste gas through the incinerator. The electrical power needed for the fan is given by the following expression:

$$Power(kW) = \frac{1.17 \times 10^{-4} \ Q_{tot} \Delta P}{\epsilon}$$

where Q_{tot} = total volumetric flow rate through the unit, 2,000 scfm here

ΔP = system pressure drop, in H_2O

ϵ = fan efficiency, taken as 0.60 here (Reference 11, p. 3-55).

ΔP is taken as 14 inches H_2O for the fixed-bed catalysts and 16 inches H_2O for the ARI fluid-bed catalysts (Reference 11, p. 3-55). The electrical power consumption is thus:

	Fixed-bed catalysts (Carus, G-43A, CK-302)	Fluid-bed catalyst (ARI)
Electrical power usage rate, kW	5.5	6.2

C. COMPARISON OF CATALYSTS

Because only the Carus catalyst showed any significant deactivation over the course of the experiments, a direct economic comparison of all catalysts over their entire life cannot be made. A direct comparison can, however, be made of the normalized operating costs of catalysts used to oxidize the same gas stream over time for which actual tests were run. Table 25 shows the total length of the runs for all catalysts tested on the three inlet gas compositions used in this study. For example, on the mixed gas stream, only the ARI catalyst (operated in a fluid-bed mode) and the CK-302 were tested, each for a different length of time. A direct comparison of the annualized costs can only be made for that period of time for which both were operated, in this case 3,096 hours (129 days).

Three economic comparisons are thus possible—one for each gas stream tested. Annualized costs are compared using the EPA's methodology (Reference 11). Input into this analysis includes the total capital investment (TCI), which is shown in Table 26 and is calculated from the equipment costs and installation factors given in Reference 11. [Capital costs are not given for the ARI catalyst operated in a fixed-bed mode, since only a fluid bed is used commercially.

TABLE 25. TOTAL RUN LENGTH FOR ALL CATALYSTS TESTED (HOURS)

Catalyst	Inlet gas[a]		
	Chlorinated	Mixed	Hydrocarbon

ARI
  fluid bed
  fixed bed
	5,712
	3,672
		4,824
		[b]
			[b]
			[b]

Carus	[b]	[b]	7,128
CK-302	5,928	3,096	[b]
UCI G-43A	[b]	[b]	5,976

[a] See Table 4 for inlet gas compositions.
[b] These runs were not made.

51

TABLE 26. TOTAL CAPITAL INVESTMENT FOR CATALYTIC INCINERATORS

	ARI (fluid bed)	Carus, UCI, Haldor/Topsoe (fixed bed)
Purchased equipment cost (PEC) Incinerator (EC) Instrumentation, taxes, freight (0.18 EC)	$ 118,200 21,300	$ 84,100 15,100
Total PEC	139,500	99,200
Direct installation costs (0.30 PEC)	35,500	25,200
Indirect installation costs (0.31 PEC)	36,600	26,100
Total capital investment, TCI	$ 211,600	$ 150,500

Auxiliary fuel costs are calculated from Equation (20). All values in this expression are known except T_{ri} and $\Delta h_{c_{wo}}$, which vary for each gas stream and catalyst. The values for T_{ri} and $\Delta h_{c_{wo}}$ that are used in the cost calculation are shown below:

Catalyst	Gas stream					
	Chlorinated		Mixed		Hydrocarbon	
	T_{ri}, °F	$\Delta h_{c_{wo}}$,[a] Btu/lb	T_{ri}, °F	$\Delta h_{c_{wo}}$,[a] Btu/lb	T_{ri}, °F	$\Delta h_{c_{wo}}$,[a] Btu/lb
ARI	679	13.7	751[b]	50.2	c	c
CK-302	751	13.7	661	50.2	c	c
Carus	c	c	c	c	d	55.8
G-43A	c	c	c	c	805	55.8

[a] Calculated as Btu/lb of incoming waste gas.

[b] Temperature required for 99 percent conversion increased rapidly from 724 °F to near 751 °F at the beginning of the run and remained near this value over the run time. A value of 751 °F is used here as representative of the temperature during the first 3,096 hours of operation.

[c] These runs were not made.

[d] Calculated from Equation (21) as a function of time on stream.

Annualized costs for the three inlet gas compositions, based on the common operating time for each, are shown in Tables 27 through 29. Not included in these tables is an annualized cost for catalyst replacement, which may be significant. [This cost cannot be evaluated because all catalysts were not tested until complete deactivation occurred. Nevertheless, replacement costs for the catalysts, based solely on the volume or weight of the catalyst and its nominal cost (but not accounting for how often it must be replaced) are given in Table 30 for the 2,000 scfm unit size considered here.]

TABLE 27. COMPARISON OF THE NORMALIZED ANNUAL OPERATING COSTS FOR ARI AND CK-302 CATALYSTS BASED ON 5,712 HOURS OPERATION–CHLORINATED STREAM

Cost item	Suggested factor	Cost	Cost unit	ARI	CK-302
Direct annual costs, DC					
Op. labor					
Operator	0.5 h/shift	12.96	$/h	4,630	4,630
Supervisor	15% op. labor			700	700
Maintenance					
Labor	0.5 h/shift	14.26	$/h	5,090	5,090
Materials	100% maint. labor			5,090	5,090
Utilities					
Natural gas		3.30	$/ft^3	16,652	18,788
Electricity			$/kWh	2,100	1,840
		0.059			
Total DC				34,262	36,138
Indirect annual costs, IC					
Overhead	60% of sum of op., supv., and maint. labor and materials			9,306	9,306
Administration	2% TCI			3,020	2,150
Property taxes	1% TCI			1,510	1,080
Insurance	1% TCI			1,510	1,080
Capital recovery	(10%/10 yr, or 16.275% of TCI)			24,590	17,490
Total IC				39,936	31,106
Total annual cost				74,198	67,244

53

TABLE 28. COMPARISON OF NORMALIZED ANNUAL OPERATING COSTS FOR CARUS AND G-43A CATALYSTS BASED ON 5,976 HOURS OPERATION–HYDROCARBON STREAM

Cost item	Suggested factor	Cost	Cost unit	CARUS	G-43A
Direct annual costs, DC					
Op. labor					
Operator	0.5 h/shift	12.96	$/h	4,840	4,840
Supervisor	15% op. labor			730	730
Maintenance					
Labor	0.5 h/shift	14.26	$/h	5,330	5,330
Materials	100% maint. labor			5,330	5,330
Utilities					
Natural gas		3.30	$/ft^3	12,570	17,980
Electricity			$/kWh	1,870	1,870
		0.059			
Total DC				30,670	36,080
Indirect annual costs, IC					
Overhead	60% of sum of op., supv., and maint. labor and materials			9,738	9,738
Administration	2% TCI			2,250	2,250
Property taxes	1% TCI			1,120	1,120
Insurance	1% TCI			1,120	1,120
Capital recovery	(10%/10 yr, or 16.275% of TCI)			18,300	18,300
Total IC				35,528	35,528
Total annual cost				63,198	68,608

54

TABLE 29. COMPARISON OF NORMALIZED ANNUAL OPERATING COSTS FC.1 ARI AND CK-302 CATALYSTS BASED ON 3,096 HOURS OPERATION–MIXED STREAM

Cost item	Suggested factor	Cost	Cost unit	ARI	CK-302
Direct annual costs, DC					
Op. labor					
Operator	0.5 h/shift	12.96	$/h	2,510	2,510
Supervisor	15% op. labor			380	380
Maintenance					
Labor	0.5 h/shift	14.26	$/h	2,760	2,760
Materials	100% maint. labor			2,760	2,760
Utilities					
Natural gas		3.30	$/ft^3	8,680	7,230
Electricity			$/kWh	2,100	1,840
		0.059			
Total DC				19,190	17,480
Indirect annual costs, IC	60% of sum of op., supv., and maint. labor and materials			5,050	5,050
Overhead					
Administration	2% TCI			1,640	1,160
Property taxes	1% TCI			820	580
Insurance	1% TCI			820	580
Capital recovery	(10%/10 yr, or 16.275% of TCI)			13,330	9,480
Total IC				21,650	16,850
Total annual cost				40,850	34,330

55

TABLE 30. CATALYST REPLACEMENT COST FOR 2,000 scfm UNIT

Catalyst	Space velocity, hr^{-1}	Catalyst replacement		Catalyst cost		Total replacement Cost
		Weight, lb^a	Volume, ft^3	\$/lb	\$/ft^3	
ARI	12,000^b	636	c	4.90	c	3,120
Carus	15,000^b	500	c	12.50	c	6,250
CK-302	3,700	c	162	c	425	13,730
G-43A	9,500	c	57	c	1,245	14,190

^{a} Calculated assuming 40 percent void space, which is the value recommended by the vendor.
^{b} These space velocities were used on both the chlorinated and mixed gas streams.
^{c} The ARI and Carus catalysts are sold by weight. The CK-302 and G-43A catalysts are sold by volume.

Because none of the catalysts were operated for more than 1 year, each of the line item costs in the "annualized" costs given in Tables 27 through 29 is normalized by actual operating time. For example, the operating labor cost for the hydrocarbon stream is calculated for an operation period of 5976 hours (per Table 25), as follows:

$$Operating\ Labor = \left(\frac{0.5\ h}{shift}\right)\left(\frac{5976\ h}{8h/shift}\right)\left(\frac{\$12.96}{h}\right)$$

$$= \$4,841$$

Similarly, all indirect costs are normalized. For example, the "Administration" line item is typically calculated as 2 percent of the TCI. For the hydrocarbon gas stream (Table 28), assuming 8,000 hours for a full operating year (as is done by EPA [Reference 11]) in calculating annual operating costs for catalytic incinerators), "Administration" costs for the fixed-bed catalysts are calculated as follows (Table 26 gives TCI):

$$Administration = (0.02)\ (\$150,500)\left(\frac{5,976\ h}{8,000\ h}\right)$$

$$= \$2,250 \quad .$$

56

A comparison of the costs in Tables 27 through 29 shows the importance of auxiliary fuel costs. For example, for the chlorinated gas stream, which has the highest natural gas usage rate (due to the low heat of combustion of the compounds in this gas), natural gas cost are 45 percent of the operating costs for the ARI catalyst and 51 percent of those for the CK-302 catalyst. For this same gas stream, note that the higher natural gas cost for the CK-302 catalyst is compensated by the lower TCI required for this fixed-bed catalyst. This lower TCI is reflected primarily in the lower capital recovery costs. The net effect is that these two catalysts, under the assumptions herein, have roughly the same operating costs.

A comparison of the Carus and G-43A catalyst (Table 28) shows that the Carus catalyst (which operated at temperatures below about 650 °F for the period of comparison) required about 30 percent less auxiliary fuel. Despite the deactivation observe d over the 5,976-hour period of comparison, the operating cost of the Carus catalyst was thus substantially less because of its lower operating temperature. Although the costs given in Table 28 do **not** include catalyst replacement costs, which would likely change the comparison of these two catalysts, it is important to note that a catalyst that deactivates is not necessarily more expensive to operate than one that does not deactivate.

An additional comparison of interest is the operating costs of the ARI and CK-302 catalysts for both chlorinated and mixed-stream oxidation. A direct comparison can be made by recalculating the costs for the chlorinated stream (Table 31) for a 3,096-hour period of operation.

The cost associated with the mixed stream for the CK-302 catalyst are somewhat lower than the other costs because of the lower operating temperature required (see Table 29) and therefore the lower auxiliary fuel costs for oxidizing the mixed stream.

TABLE 31. TOTAL COSTS FOR 3,096 HOURS OPERATION

Catalyst	Chlorinated stream	Mixed stream
ARI	$ 48,780	$ 40,850
CK-302	$ 47,800	$ 34,330

SECTION VII

CONCLUSIONS AND RECOMMENDATIONS

A. CONCLUSIONS

Four commercial oxidation catalysts were evaluated in this work for an extended period of time using air streams containing VOCs typical of those expected from Air Force groundwater air strippers. Three different air streams--hydrocarbons, chlorinated, and mixed stream--were used in this study. Two catalysts, a noble metal catalyst (UCI G-43A) and a mixed metal oxide catalyst (Carus), were evaluated for the oxidation of hydrocarbons containing stream. Similarly, two mixed-metal oxide catalysts, ARI and CK-302, were evaluated for the oxidation of chlorinated stream. These two catalysts were also investigated for the oxidation of mixed stream.

The catalysts were used for the oxidation of 500 ppm of organics using vendor-recommended space velocity and initial reaction temperature. The oxidation reaction was conducted at constant total conversion (>99 percent) and the reaction temperature was increased, when necessary, to compensate for the loss of any catalyst activity.

The UCI catalyst, used for hydrocarbon oxidation, did not lose any catalyst activity when used for 201 days on stream. In addition, the selectivity of the catalyst did not change during this time. The only oxidation products formed over this catalyst were CO_2 and H_2O. A visual observation of the used catalyst showed black spots in the catalyst bed which is believed to be the carbide phase that is active for VOC oxidation.

The Carus catalyst, also used for hydrocarbon oxidation, lost significant activity during 297 days on stream. The temperature had to be increased by 87 °C during this time to maintain the total conversion above 99 percent. Interestingly, the selectivity of the catalyst did not change during this time as seen by the absence of any partial oxidation products. Furthermore, only CO_2 was formed over this catalyst, as in the case of G-43A catalyst. A simple first-order deactivation model was fit to the experimental activity data over the Carus catalyst. This model predicts a catalyst lifetime of 362 days, assuming the maximum operating temperature for this catalyst is 500 °C.

The CK-302 catalyst used for the oxidation of both chlorinated and mixed streams did not lose any activity. The catalyst for the oxidation of chlorinated stream was operated for 247 days while the catalyst used for mixed stream oxidation was operated for 129 days. A higher initial temperature (400 °C) was required than recommended by the vendor (350 °C) for the oxidation of chlorinated stream. This is because of the formation of significant amounts of partial oxidation product, namely 1,1,2-trichloroethane. In addition, a small amount of chloroform was also formed over this catalyst. Although some partial oxidation products were formed over this catalyst, the total oxidation

products contained only CO_2 (and no CO). Both HCl and Cl_2 were formed over this catalyst, with Cl_2 accounting for less than 5 percent.

The ARI catalyst was also evaluated for the oxidation of both chlorinated and mixed stream. The oxidation of mixed stream using this catalyst was studied in both the fixed-bed and the fluid-bed reactor to investigate the effect of reactor type on catalyst activity. The catalyst used for the oxidation of chlorinated stream did not lose any significant activity when used for 153 days on stream in the fixed-bed reactor. As in the case of CK-302 catalyst, some partial oxidation products were formed over this catalyst. The deep oxidation products contained both CO and CO_2. In fact, the CO/CO_2 ratio, a measure of the oxidation power of the catalyst, increased from 0.47 at the start of the run to 1.17 at the end of 153 days. Also, a distinct color change was observed from the dowstream to the upstream of the bed. Although the overall activity of the catalyst did not change with time on stream, the catalyst did suffer some activity loss across the bed. As the front portion of the catalyst bed deactivates, the reaction zone probably moves progressively down the bed until the bed exit is reached. Thus, although part of the catalyst has apparently deactivated, the overall conversion would not change until the reaction zone reached the bed exit, at which point the total conversion would rapidly decrease.

Similar to the fixed-bed operation, the ARI catalyst used for the chlorinated stream oxidation in the fluid-bed operation did not lose any appreciable activity when used for 196 days on stream. However, the ARI catalyst used for mixed-stream oxidation in the fluid-bed reactor did deactivate and required a temperature increase of 33 °C over 210 days on stream to maintain a constant conversion. The BET surface area of the catalyst used for mixed stream oxidation decreased by 20 percent, suggesting that some catalyst sintering occurred during reaction and may be responsible for activity loss. The BET surface area of the catalyst used for chlorinated stream oxidation did not change.

A detailed economic analysis was conducted to compare the cost of operation of different catalysts. The replacement cost is higher for G-43A than for Carus catalyst for the oxidation of hydrocarbon stream. This cost is based on vendor-recommended space velocity and per-unit catalyst cost. Comparing operating costs shows that this cost is the highest for G-43A for oxidation of hydrocarbons. These data are based on 250 days of operation. Depending on the rate of catalyst deactivation after 250 days on stream, the relative operating cost of the two catalysts may change. For the oxidation of mixed stream, the operating cost for ARI catalyst is higher than for CK-302 catalyst. Again, this conclusion is based on 129 days of operation. The operating costs of CK-302 and ARI catalysts for the oxidation of chlorinated stream are comparable for 238 days of operation.

B. RECOMMENDATIONS

Based on the results obtained in this work, the catalysts can be ranked for optimum performance and economics as shown in Table 32.

It should be noted that none of the catalysts completely deactivated in the timeframe of these experiments. The conclusions drawn in Table 32 might change if the rate of catalyst deactivation were to significantly change after this time.

Both the operation and replacement costs for Carulite catalyst are lower than for the G-43A catalyst suggesting that the former is better for hydrocarbon oxidation. The operating costs of CK-302 and ARI

TABLE 32. OPTIMUM CATALYST FOR VOC OXIDATION

	Oxidation of		
	Hydrocarbon	Chlorocarbon	Mixed
G-43A	2	-	-
Carulite	1	-	-
ARI	-	1	2
CK-302	-	2	1

catalysts for chlorinated stream oxidation were similar. However, the replacement cost of ARI catalyst is only 23 percent of the CK-302 catalyst making ARI the better catalyst for chlorinated stream oxidation. The operating cost of CK-302 catalyst is lower than ARI for the oxidation of mixed stream. The deactivation trend of ARI catalyst for the mixed stream oxidation suggests the operating costs for this catalyst would rise relatively significantly with time on stream. Thus, the higher replacement cost of CK-302 catalyst would be more than compensated for by its lower operation cost for the oxidation of mixed stream.

Future research efforts should be concentrated on developing more reliable analytical methods for HCl and Cl_2 measurements. The results obtained using the Dräger tubes and impinger methods in this work were not very accurate. As a result, the chlorine balance could not be closed. The ability to close the mass balance on chlorine will be very useful in understanding the catalyst deactivation mechanisms.

The use of chromia alumina catalyst in the fluidized-bed reactor for chlorinated stream oxidation results in the loss of chromium from the catalyst. The environmental implications of such chromium loss should be considered from a commercial oxidizer.

This study was conducted using gas stream free of dust and other solid particles which may be present in gas stream from Air Force strippers. The dust and solid particles can cause catalyst deactivation and should be considered for the operation of a commercial oxidizer.

This study was conducted in a laboratory scale reactor. In a commercial reactor using larger particles, significant pore diffusion can occur resulting in reduced conversion. The presence of pore diffusion should be considered for the operation of a commercial scale oxidizer.

REFERENCES

1. Hardison, L.C., and E.J. Dowd, "Emission Control Via Fluidized Bed Oxidation," *CEP*, 1977, p. 31.

2. Wasfi, A.K., G.P. Mathur, C.C. St. Pierre, and A.W. Gnyp, *Atmospheric Environ.,* 1978, vol. 12, p. 2389.

3. Spivey, J.J., "Complete Catalytic Oxidation of Volatile Organics," *IEC Res.*, vol. 26, p. 2165.

4. Kosusko, M., M.E. Mullins, K. Ramanathan, and T.N. Rogers, "Catalytic Oxidation of Groundwater Stripping Emissions," *Environ. Prog.*, 1988, vol. 7, p. 136.

5. Cheuvront, D.A., C.L. Giggy, C.G. Loven, and Swett, G.H., "Groundwater Treatment with Zero Air Emissions." *Environ. Prog.*, vol. 9, p. 143.

6. Weldon, J., and S.M. Senkan, "Catalytic Oxidation of CH_3Cl by Cr_2O_3" *Combust. Sci. Technol.*, 1986, vol. 47, p. 229.

7. Stallings, R.L., and T.N. Rogers, "Packed Tower Aeration Study to Remove Volatile Organics from Groundwater at Wurtsmith AFB," 1984, Draft report.

8. Hughes, R., *Deactivation of Catalysts*, Academic Press, New York, 1984, p. 51.

9. Voorhies, A., *IEC*, 1954, vol. 37, p. 318.

10. Szepe, S., and O. Levenspiel, Proc. 4th Europ. Symp. Chem. React. Eng., Pergamon Press, p. 265.

11. U.S. Environmental Protection Agency, OAQPS Control Cost Manual, EPA-450/3-90-006, U.S. EPA, OAQPS (Research Triangle Park, NC), 1990, pp. 3-1 - 3-64.

12. Agarwal, S.K., Private communications with UCI, ARI, and Carus Chemical Company, 1990.

13. Gangwal, S.K., M.E. Mullins, J.J. Spivey, and P.R. Caffrey, "Kinetics and Selectivity of Deep Catalytic Oxidation of n-Hexane and Benzene," *Appl. Catal.*, vol. 36, 1988, p. 231.

14. Musick, J.K., F.S. Thomas, and J.E. Johnson, "Catalytic Oxidation Studies in the Vapor Phase Using Axial Sampling of the Bed," *IEC Proc. Des. Develop.*, vol. 11, 1972, p. 350.

14. Musick, J.K., F.S. Thomas, and J.E. Johnson, "Catalytic Oxidation Studies in the Vapor Phase Using Axial Sampling of the Bed," *IEC Proc. Des. Develop.*, vol. 11, 1972, p. 350.

15. Ramanathan, K., and J.J. Spivey, 1988, Research Triangle Institute (Research Triangle Park, NC), unpublished results.

16. Young, P.D., M.S. Thesis, "A Kinetic Study of the Catalytic Oxidation of Dichloromethane," MIT, Cambridge, MA, June 1982.

17. Wilson, J.H., R.M. Counce, A.J. Lucero, H.L. Jennings, and S.P. Singh, "Air Stripping and Emissions Control Technologies. Field Testing of Countercurrent Packings, Rotary Air Stripping, Catalytic Oxidation, and Adsorption Materials," AFESC TR-90-51, Tyndall AFB FL, in publication.

APPENDIX A

ACTIVITY TABLES

Table A-1. Hydrocarbons Conversion Over G-43A Catalyst

Time days	Temp	Pentane	2,3 Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	Total
0	430	98.3	99.4	>99.9	>99.9	99.9	99.6	>99.9	99.9	99.6
2	430	99.7	>99.9	>99.9	>99.9	>99.9	99.9	99.9	>99.9	99.9
3	430	99.6	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9
4	430	99.6	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9
5	430	99.5	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.9
8	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
9	430	>99.9	99.7	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
10	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
11	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
12	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
13	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
14	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
15	430	99.9	>99.9	99.7	99.9	99.6	>99.9	99.5	>99.9	99.9
16	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
17	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
18	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
19	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.7	>99.9
20	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
21	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
22	430	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	99.9	>99.9	>99.9
23	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
24	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
25	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
26	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.4	>99.9
31	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
32	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
33	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
34	430	99.8	99.6	99.8	99.9	99.7	99.8	99.7	>99.9	99.8
36	430	99.8	98.3	>99.9	>99.9	98.3	99.9	99.9	>99.9	99.8
37	430	99.6	97.7	>99.9	>99.9	98.6	99.9	>99.9	>99.9	99.8
38	430	99.7	98.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	99.9
39	430	99.6	99.1	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	99.9
40	430	99.7	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9
41	430	99.8	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.9
42	430	99.7	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.9
43	430	99.6	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9
44	430	99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
48	430	99.8	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
49	430	99.8	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
50	430	99.4	99.1	99.5	99.6	99.1	98.4	97.8	92.5	99.0
55	430	99.6	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9
56	430	99.5	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9
57	430	99.1	98.9	>99.9	>99.9	98.0	99.9	99.9	>99.9	99.7
58	430	99.9	99.7	>99.9	>99.9	99.6	99.7	99.8	>99.9	99.9
61	430	98.5	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.7
62	430	99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
63	430	99.9	99.3	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	99.9
64	430	99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
65	430	99.4	99.4	99.4	99.5	99.1	98.7	98.5	>99.9	99.2
66	430	99.8	>99.9	99.9	99.9	99.8	99.7	99.7	98.4	99.8
67	430	99.9	>99.9	99.9	>99.9	99.8	99.8	99.8	>99.9	99.9
69	430	99.8	>99.9	99.8	>99.9	99.9	99.9	99.9	>99.9	99.9
70	430	99.7	>99.9	99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.9
71	430	99.7	98.4	99.5	99.8	99.3	99.8	99.8	>99.9	99.7
76	430	99.2	99.2	99.3	99.3	98.6	97.7	97.1	>99.9	98.8
77	430	99.8	>99.9	99.6	99.9	99.5	99.4	99.3	98.1	99.7
78	430	99.9	>99.9	>99.9	99.9	99.6	99.7	99.7	99.8	99.8
79	430	99.8	>99.9	>99.9	>99.9	99.4	99.9	99.9	>99.9	99.9
80	430	99.9	>99.9	>99.9	>99.9	99.8	99.9	99.9	>99.9	99.9
81	430	99.9	>99.9	>99.9	>99.9	99.8	99.9	99.9	>99.9	99.9
82	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	>99.9
83	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	>99.9
84	430	99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	>99.9
85	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	>99.9
86	430	99.9	>99.9	>99.9	>99.9	99.8	>99.9	99.9	>99.9	>99.9

Table A-1 (continued)

Time days	Temp	Pentane	2,3 Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	Total
87	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
88	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
89	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	>99.9
90	430	98.4	98.0	98.3	98.2	97.7	98.7	98.9	>99.9	98.4
91	430	99.2	98.8	99.1	99.3	98.7	98.8	99.1	>99.9	99.2
92	430	97.3	97.9	97.0	97.5	94.7	90.9	89.1	92.7	95.4
93	430	98.1	98.5	>99.9	>99.9	96.2	93.6	92.9	95.9	97.7
94	430	99.7	>99.9	99.7	99.7	99.1	98.3	98.1	98.9	99.3
95	430	99.9	>99.9	99.9	99.9	99.5	99.3	99.1	93.4	99.7
96	430	99.8	99.3	99.8	99.9	98.3	99.0	98.8	99.1	99.5
97	430	>99.9	>99.9	99.9	99.9	99.4	99.5	99.4	99.6	99.8
98	430	99.9	>99.9	99.9	>99.9	99.7	>99.9	99.8	99.7	99.9
99	430	>99.9	>99.9	>99.9	>99.9	99.9	99.9	99.9	>99.9	>99.9
100	430	99.9	>99.9	>99.9	>99.9	99.8	98.8	99.7	>99.9	99.9
101	430	>99.9	>99.9	>99.9	>99.9	99.8	99.9	99.7	>99.9	99.9
102	430	99.9	>99.9	>99.9	>99.9	>99.9	99.8	99.7	99.8	99.9
103	430	99.5	99.2	99.5	99.7	98.7	98.4	97.3	97.7	99.0
104	430	99.9	>99.9	99.8	99.9	99.6	99.6	99.5	99.6	99.8
105	430	>99.9	>99.9	>99.9	>99.9	99.9	99.9	99.9	>99.9	>99.9
106	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	>99.9
107	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	>99.9
108	430	>99.9	>99.9	>99.9	>99.9	99.8	99.8	99.8	>99.9	99.9
109	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	99.9
114	430	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	99.9	>99.9	99.9
115	430	99.9	>99.9	>99.9	>99.9	99.6	99.9	99.9	>99.9	99.9
118	430	>99.9	>99.9	>99.9	>99.9	99.8	99.7	99.6	99.6	99.9
119	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9
120	430	>99.9	>99.9	>99.9	>99.9	99.8	99.9	99.9	>99.9	>99.9
121	430	>99.9	>99.9	>99.9	>99.9	99.9	99.9	99.9	>99.9	>99.9
122	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9
123	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9
124	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
125	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
127	430	99.9	>99.9	99.9	99.9	99.5	98.7	98.4	99.0	99.5
128	430	>99.9	>99.9	>99.9	>99.9	99.9	99.9	99.8	>99.9	99.9
129	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9
130	430	>99.9	>99.9	>99.9	>99.9	>99.9	99.5	>99.9	>99.9	>99.9
131	430	>99.9	>99.9	>99.9	>99.9	99.9	99.9	99.9	>99.9	>99.9
132	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
133	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
134	430	>99.9	>99.9	>99.9	>99.9	>99.9	99.7	99.3	>99.9	99.9
135	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
136	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
137	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
138	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
139	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
140	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
141	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
143	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
144	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
146	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
147	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
148	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
149	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
150	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
152	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
153	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
156	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
159	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
160	430	>99.9	>99.9	>99.9	>99.9	99.5	>99.9	>99.9	>99.9	>99.9
161	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
162	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
163	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
164	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
165	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9

Time days	Temp	Pentane	2,3 Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	Total
166	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
167	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
168	430	99.9	>99.9	>99.9	99.9	99.8	99.6	99.5	99.6	99.8
169	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
170	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
171	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
172	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
173	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
174	430	>99.9	>99.9	>99.9	>99.9	99.6	99.8	99.7	>99.9	99.9
175	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
176	430	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
177	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
178	430	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
179	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
180	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
181	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
182	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
183	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>59.9	>99.9
184	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
185	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
186	430	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
187	430	>99.9	99.5	>99.9	>99.9	99.3	>99.9	>99.9	>99.9	>99.9
188	430	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	>99.9
189	430	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
190	430	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
191	430	>99.9	>99.	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
192	430	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	>99.9
193	430	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
190	430	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
191	430	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	>99.9
192	430	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	>99.9
193	430	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>59.9	>99.9	>99.9
204	430	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	>99.9
205	430	99.9	>99.9	>99.9	>99.9	99.4	>99.9	>99.9	>99.9	99.9
206	430	>99.9	>99.9	>99.9	>99.9	99.5	>99.9	>99.9	>99.9	>99.9
207	430	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	>99.9
208	430	99.3	99.5	99.5	99.4	98.4	97.7	97.4	97.8	98.8
209	430	99.9	>99.9	99.9	99.9	99.5	99.7	99.7	99.6	99.8
211	430	99.9	>99.9	99.9	99.9	99.7	99.3	99.1	99.3	99.7
212	430	99.9	>99.9	>99.9	>99.9	99.2	>99.9	99.8	>99.9	99.9
213	430	99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	99.8	>99.9
214	430	>99.9	>99.9	>99.9	>99.9	99.9	99.9	99.9	>99.9	99.9
217	430	>99.9	>99.9	>99.9	>99.9	99.9	99.9	99.9	>99.9	99.9
218	430	99.9	>99.9	>99.9	>99.9	99.6	99.9	>99.9	>99.9	>99.9
219	430	99.9	99.6	99.9	>99.9	98.2	99.8	99.9	>99.9	99.8
220	430	99.9	99.7	99.9	99.9	98.1	99.9	99.9	>99.9	99.8
221	430	99.9	>99.9	>99.9	>99.9	99.1	>99.9	99.9	>99.9	99.9
222	430	>99.9	>99.9	>99.9	>99.9	99.3	>99.9	>99.9	>99.9	99.9
224	430	>99.9	>99.9	>99.9	>99.9	99.4	>99.9	>99.9	>99.9	>99.9
226	430	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	>99.9
227	430	99.9	>99.9	>99.9	>99.9	99.3	>99.9	>99.9	>99.9	99.9
228	430	99.9	>99.9	>99.9	>99.9	99.2	>99.9	>99.9	>99.9	99.9
231	430	99.9	99.5	>99.9	>99.9	98.6	>99.9	>99.9	>99.9	99.9
232	430	99.9	98.6	>99.9	>99.9	98.9	>99.9	>99.9	>99.9	99.9
233	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
235	430	>99.9	>99.9	98.7	>99.9	>99.9	99.5	>99.9	>59.9	99.9
236	430	99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
237	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
238	430	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
239	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
240	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
242	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
243	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
244	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
245	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9

Time days	Temp	Pentane	2,3 Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	Total
246	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.5	>99.9
247	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	98.7	>99.9
248	430	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
249	430	>99.9	>99.9	>99.9	>99.9	>59.9	>99.9	>99.9	99.5	>99.9

Table A-2. Hydrocarbons Conversions Over Carulite Catalyst

Time days	Temp C	Pentane	2,3 Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	Total
3	315	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.4	>99.9
4	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.4	>99.9
5	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.3	>99.9
8	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.5	>99.9
9	315	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	99.1	>99.9
10	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	98.6	>99.9
11	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	98.6	>99.9
12	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	98.1	>99.9
13	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	97.7	>99.9
14	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.3	>99.9
15	315	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
16	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	98.2	>99.9
17	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	93.2	99.9
18	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.3	>99.9
19	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	95.4	99.9
20	315	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
21	315	99.8	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	99.9
22	315	99.5	99.9	>99.9	>99.9	99.2	>99.9	99.9	>99.9	99.8
23	315	99.3	>99.9	>99.9	>99.9	98.5	>99.9	>99.9	>99.9	99.8
24	315	99.2	>99.9	>99.9	>99.9	98.0	>99.9	>99.9	>99.9	99.7
25	315	99.3	>99.9	>99.9	>99.9	98.5	>99.9	>99.9	>99.9	99.8
26	315	99.3	>99.9	>99.9	>99.9	98.3	>99.9	>99.9	>99.9	99.8
27	315	99.5	>99.9	>99.9	>99.9	98.9	>99.9	>99.9	>99.9	99.8
28	315	99.8	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	99.9
29	315	98.8	>99.9	>99.9	>99.9	96.6	>99.9	>99.9	>99.9	99.5
30	315	99.0	>99.9	>99.9	>99.9	97.0	>99.9	>99.9	>99.9	99.6
31	315	98.8	>99.9	>99.9	>99.9	96.4	>99.9	>99.9	>99.9	99.5
32	315	98.6	>99.9	>99.9	>99.9	95.5	>99.9	>99.9	>99.9	99.5
33	315	99.1	>99.9	>99.9	>99.9	97.8	>99.9	>99.9	>99.9	99.7
34	315	98.0	99.5	99.9	99.9	93.8	99.8	99.8	>99.9	98.9
36	315	96.0	98.5	99.9	99.8	82.0	>99.9	99.9	>99.9	97.8
37	323	98.0	99.5	>99.9	99.9	92.6	>99.9	>99.9	>99.9	99.0
38	323	97.7	99.4	>99.9	>99.9	91.7	>99.9	>99.9	>99.9	98.9
39	323	97.4	99.5	99.9	99.9	89.9	>99.9	>99.9	>99.9	98.7
40	328	98.4	99.7	>99.9	>99.9	95.4	>99.9	>99.9	>99.9	99.3
41	328	98.7	99.9	>99.9	>99.9	96.5	>99.9	>99.9	>99.9	99.6
42	328	98.4	99.9	>99.9	>99.9	95.8	>99.9	>99.9	>99.9	99.3
43	328	99.0	>99.9	>99.9	>99.9	97.3	>99.9	>99.9	>99.9	99.6
44	328	98.9	>99.9	>99.9	>99.9	98.0	>99.9	>99.9	>99.9	99.6
48	328	99.1	99.8	>99.9	>99.9	97.3	>99.9	>99.9	>99.9	99.6
49	328	99.1	>99.9	>99.9	>99.9	97.6	>99.9	>99.9	>99.9	99.5
50	328	98.6	99.6	99.7	99.8	96.0	99.1	99.8	>99.9	99.0
55	328	98.6	>99.9	>99.9	>99.9	95.5	>99.9	>99.9	>99.9	99.1
56	328	98.3	99.7	>99.9	>99.9	94.2	>99.9	>99.9	>99.9	99.3
57	328	97.6	98.9	>99.9	99.9	90.2	>99.9	99.9	>99.9	98.9
58	332	98.7	99.5	>99.9	>99.9	95.2	>99.9	>99.9	>99.9	99.4
61	332	98.6	>99.9	>99.9	>99.9	95.7	>99.9	>99.9	>99.9	99.4
62	332	99.2	>99.9	>99.9	>99.9	97.8	>99.9	>99.9	>99.9	99.7
63	332	98.9	99.5	>99.9	>99.9	96.5	>99.9	>99.9	>99.9	99.6
64	332	98.8	>99.9	>99.9	>99.9	95.8	>99.9	>99.9	>99.9	99.5
65	332	98.6	99.4	99.7	99.7	95.6	99.2	99.0	96.8	99.0
66	332	98.7	>99.9	99.9	99.9	95.8	99.8	99.7	98.4	99.4
67	332	98.5	>99.9	99.9	99.9	94.5	>99.9	99.8	>99.9	99.3
69	332	98.4	99.0	99.9	99.9	94.0	99.9	99.8	>99.9	99.2
70	332	98.4	98.7	99.8	99.9	93.6	99.9	99.9	>99.9	99.2
71	332	98.6	99.5	99.7	99.8	94.7	99.8	99.8	>99.9	99.3
76	332	98.3	99.4	99.6	99.6	93.6	98.4	98.0	93.4	98.5
77	332	98.7	99.6	99.9	99.9	94.4	99.5	99.4	97.4	99.2
78	332	98.5	99.7	99.9	99.9	93.1	>99.9	99.8	99.7	99.2
79	332	98.7	>99.9	>99.9	99.9	94.5	99.8	99.8	>99.9	99.3
80	332	98.7	>99.9	>99.9	>99.9	94.3	>99.9	99.9	>99.9	99.4
81	332	98.9	>99.9	>99.9	99.9	95.7	99.9	99.9	>99.9	99.5
82	332	99.0	>99.9	>99.9	>99.9	96.6	99.9	99.9	>99.9	99.6
83	332	99.0	>99.9	>99.9	>99.9	96.4	>99.9	99.9	>99.9	99.6

68

Time days	Temp C	Pentane	2,3 Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	Total
84	332	98.8	>99.9	>99.9	>99.9	95.6	>99.9	99.9	>99.9	99.5
85	332	98.6	99.7	>99.9	>99.9	94.0	>99.9	99.9	>99.9	99.3
86	332	98.7	>99.9	>99.9	>99.9	94.4	>99.9	99.9	>99.9	99.4
87	332	98.6	99.5	>99.9	>99.9	94.4	>99.9	>99.9	>99.9	99.4
88	332	98.5	99.6	>99.9	>99.9	93.6	>79.9	>99.9	>99.9	99.3
89	332	98.4	99.5	>99.9	>99.9	93.0	99.9	99.9	>99.9	99.2
90	332	98.1	99.0	99.0	98.9	94.7	99.0	99.2	>99.9	98.6
91	332	98.5	99.5	99.6	99.6	94.9	99.2	99.3	>99.9	99.1
92	332	97.4	99.3	98.4	98.7	92.2	94.7	93.7	95.9	96.9
93	332	98.0	99.3	99.0	99.1	92.8	95.7	95.2	96.9	97.6
94	332	98.8	>99.9	99.8	99.8	94.8	98.8	98.6	99.0	99.0
95	332	98.9	>99.9	99.8	99.9	94.8	99.1	99.0	99.4	99.2
96	332	99.0	99.4	99.9	99.9	95.0	99.4	99.2	99.4	99.3
97	332	98.9	99.7	99.9	99.9	94.9	99.6	99.5	99.7	99.3
98	332	98.7	99.5	99.9	99.9	96.0	99.8	99.7	99.7	99.4
99	332	98.8	>99.9	>99.9	>99.9	95.9	99.9	99.9	>99.9	99.5
100	332	98.9	>99.9	>99.9	>99.9	95.4	99.7	99.7	>99.9	99.4
101	332	98.8	99.0	99.7	99.9	95.1	99.8	99.7	>99.9	99.4
102	332	98.5	99.7	99.9	99.9	93.4	99.8	99.8	>99.9	99.2
103	332	98.6	99.4	98.8	99.8	94.5	99.2	98.6	98.9	99.0
104	332	98.2	98.3	99.7	99.9	92.2	99.8	99.7	>99.9	99.0
105	332	98.7	90.4	>99.9	99.9	94.5	99.9	99.8	>99.9	99.3
106	332	99.1	>99.9	>99.9	>99.9	95.3	>99.9	>99.9	>99.9	99.5
107	332	99.2	>99.9	>99.9	>99.9	95.3	>99.9	99.9	>99.9	99.5
108	332	99.0	>99.9	>99.9	>99.9	95.0	>99.9	99.9	>99.9	99.5
109	332	99.1	>99.9	>99.9	>99.9	94.4	>99.9	99.9	>99.9	99.4
114	332	98.9	99.7	>99.9	>99.9	94.9	>99.9	99.9	>99.9	99.4
115	332	98.8	>99.9	>99.9	>99.9	94.1	>99.9	99.9	>99.9	99.4
116	332	98.4	99.5	>99.9	99.9	92.2	99.9	99.8	>99.9	99.1
119	332	99.1	>99.9	>99.9	>99.9	95.8	>99.9	>99.9	>99.9	99.5
120	332	99.2	>99.9	>99.9	>99.9	96.5	>99.9	>99.9	>99.9	99.6
121	332	98.9	99.8	>99.9	>99.9	94.7	>99.9	99.9	>99.9	99.4
122	332	98.2	99.5	>99.9	99.9	90.3	>99.9	>99.9	>99.9	99.0
123	332	98.4	99.2	>99.9	>99.9	91.7	>99.9	99.9	>99.9	99.2
124	332	99.1	>99.9	>99.9	>99.9	96.0	>99.9	>99.9	>99.9	99.6
125	332	99.0	>99.9	>99.9	>99.9	95.4	>99.9	>99.9	>99.9	99.5
127	332	98.7	99.7	99.9	99.9	94.3	99.4	99.3	99.3	99.2
128	332	98.8	>99.9	>99.9	>99.9	94.3	99.9	99.8	>99.9	99.4
129	332	98.9	>99.9	>99.9	>99.9	94.9	>99.9	99.9	>99.9	99.4
130	332	98.7	>99.9	>99.9	>99.9	93.3	>99.9	>99.9	>99.9	99.3
131	332	98.6	>99.9	>99.9	>99.9	93.4	>99.9	99.9	>99.9	99.3
132	332	99.1	>99.9	>99.9	>99.9	96.0	>99.9	99.9	>99.9	99.5
133	332	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
134	332	98.5	>99.9	>99.9	>99.9	92.4	>99.9	>99.9	>99.9	99.2
135	332	98.7	>99.9	>99.9	>99.9	94.4	>99.9	>99.9	>99.9	99.4
136	332	98.8	>99.9	>99.9	>99.9	93.6	>99.9	>99.9	>99.9	99.4
137	332	98.7	>99.9	>99.9	>99.9	93.6	>99.9	99.9	>99.9	99.3
138	332	98.8	99.7	>99.9	>99.9	94.1	>99.9	>99.9	>99.9	99.4
139	332	98.7	99.7	>99.9	>99.9	93.6	>99.9	99.9	>99.9	99.3
140	332	98.3	99.6	>99.9	>99.9	91.5	>99.9	>99.9	>99.9	99.1
141	332	98.5	>99.9	>99.9	>99.9	92.8	>99.9	>99.9	>99.9	99.2
143	332	98.5	99.8	>99.9	>99.9	92.7	>99.9	>99.9	>99.9	99.2
144	332	98.5	>99.9	>99.9	>99.9	92.3	>99.9	>99.9	>99.9	99.2
146	332	98.0	99.7	>99.9	99.9	88.9	>99.9	>99.9	>99.9	98.9
147	332	97.9	99.7	>99.9	99.9	89.3	>99.9	>99.9	>99.9	98.9
148	333	98.5	99.7	>99.9	>99.9	93.3	>99.9	99.9	>99.9	99.3
149	333	98.6	>99.9	>99.9	>99.9	93.8	>99.9	>99.9	>99.9	99.3
150	333	98.4	99.7	>99.9	>99.9	92.4	>99.9	>99.9	>99.9	99.2
152	333	98.4	99.7	>99.9	>99.9	92.4	>99.9	>99.9	>99.9	99.2
153	333	98.5	>99.9	>99.9	>99.9	92.6	>99.9	>99.9	>99.9	99.2
154	333	98.2	99.7	>99.9	>99.9	90.5	>99.9	>99.9	>99.9	99.0
157	333	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
158	333	98.6	>99.9	>99.9	>99.9	93.6	>99.9	>99.9	>99.9	99.3
159	333	98.7	>99.9	>99.9	>99.9	94.5	>99.9	>99.9	>99.9	99.4

Time days	Temp C	Pentane	2,3 Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	o-xene	Total
160	333	98.3	99.6	>99.9	>99.9	92.1	>99.9	>99.9	>99.9	99.2
161	333	98.7	>99.9	>99.9	>99.9	94.0	>99.9	>99.9	>99.9	99.4
162	333	98.2	99.0	>99.9	>99.9	91.4	>99.9	>99.9	>99.9	99.1
163	333	98.6	>99.9	>99.9	>99.9	92.8	>99.9	>99.9	>99.9	99.3
164	333	98.6	>99.9	>99.9	>99.9	93.6	>99.9	>99.9	>99.9	99.3
165	333	98.6	>99.9	>99.9	>99.9	93.2	>99.9	>99.9	>99.9	99.3
166	333	98.5	99.6	>99.9	>99.9	92.9	99.9	99.9	>99.9	99.2
167	333	98.5	99.7	>99.9	>99.9	92.6	>99.9	>99.9	>99.9	99.2
168	333	97.9	99.5	>99.9	99.9	88.6	>99.9	>99.9	>99.9	98.8
169	333	98.2	>99.9	>99.9	>99.9	90.6	>99.9	>99.9	>99.9	99.0
170	333	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	>99.9
171	334	98.5	99.5	>99.9	>99.9	93.2	>99.9	>99.9	>99.9	99.3
172	334	97.9	99.6	>99.9	99.9	89.0	>99.9	99.9	>99.9	98.9
173	335	98.6	>99.9	>99.9	>99.9	93.2	>99.9	>99.9	>99.9	99.3
174	335	98.1	99.7	>99.9	>99.9	89.8	>99.9	>99.9	>99.9	99.0
175	336	97.9	99.6	>99.9	99.9	88.7	>99.9	>99.9	>99.9	98.9
176	336	98.1	99.7	>99.9	99.9	89.9	>99.9	>99.9	>99.9	99.0
177	336	98.6	>99.9	>99.9	>99.9	93.1	>99.9	>99.9	>99.9	99.3
178	336	98.7	>99.9	>99.9	>99.9	93.3	>99.9	>99.9	>99.9	99.3
179	336	98.1	99.7	>99.9	>99.9	90.3	>99.9	>99.9	>99.9	99.0
180	336	98.2	99.6	>99.9	>99.9	90.8	>99.9	>99.9	>99.9	99.0
181	337	98.2	99.6	>99.9	>99.9	90.3	>99.9	>99.9	>99.9	99.0
182	337	98.6	>99.9	>	>99.9	93.8	>99.9	>99.9	>99.9	99.3
183	337	98.5	>99.9	>99.9	>99.9	93.1	>99.9	>99.9	>99.9	99.3
184	337	98.0	99.7	>99.9	99.9	89.5	>99.9	>99.9	>99.9	98.9
185	337	98.5	99.5	>99.9	>99.9	92.3	>99.9	>99.9	>99.9	99.2
186	337	98.2	99.7	>99.9	>99.9	92.5	>99.9	>99.9	>99.9	99.0
187	338	98.3	99.7	>99.9	>99.9	91.4	>99.9	>99.9	>99.9	99.1
188	338	98.3	99.6	>99.9	>99.9	91.5	>99.9	>99.9	>99.9	99.1
189	338	98.4	99.7	>99.9	>99.9	92.0	99.9	>99.9	>99.9	99.2
190	338	98.4	99.7	>99.9	>99.9	91.8	>99.9	>99.9	>99.9	99.1
191	338	98.3	99.7	>99.9	>99.9	91.3	>99.9	>99.9	>99.9	99.1
202	340	98.7	>99.9	>99.9	>99.9	93.6	>99.9	>99.9	>99.9	99.3
203	340	98.6	99.5	>99.9	>99.9	93.3	>99.9	>99.9	>99.9	99.3
204	340	98.8	>99.9	>99.9	>99.9	94.0	>99.9	>99.9	>99.9	99.4
205	340	98.6	99.0	>99.9	>99.9	93.4	>99.9	>99.9	>99.9	99.3
206	340	98.7	99.6	99.7	99.7	94.4	98.7	98.5	98.5	98.9
207	340	98.9	99.8	99.9	>99.9	94.5	99.9	99.9	>99.9	99.4
209	340	96.3	99.1	99.8	99.8	77.5	99.5	99.4	99.4	97.6
210	340	97.3	99.2	99.8	99.8	87.3	>99.9	99.7	99.6	98.5
211	341	96.4	99.3	>99.9	99.8	79.0	99.8	99.8	99.7	97.9
212	341	96.4	99.1	99.9	99.8	79.7	99.9	99.9	>99.9	97.9
215	341	>99.9	>99.9	>99.9	>99.9	99.3	99.8	>99.9	>99.9	99.9
216	341	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9
217	341	>99.9	>99.9	>99.9	>99.9	99.2	99.9	99.9	>99.9	99.9
218	341	99.9	>99.9	>99.9	>99.9	99.4	99.9	99.9	>99.9	99.9
219	341	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	>99.9
220	341	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	>99.9
222	342	98.6	>99.9	>99.9	>99.9	92.1	>99.9	>99.9	>99.9	99.2
224	342	98.9	>99.9	>99.9	>99.9	94.1	>99.9	>99.9	>99.9	99.4
225	342	99.1	>99.9	>99.9	>99.9	94.9	>99.9	>99.9	>99.9	99.5
226	342	99.1	>99.9	>99.9	>99.9	95.9	>99.9	>99.9	>99.9	99.6
229	342	99.1	>99.9	>99.9	>99.9	95.9	>99.9	>99.9	>99.9	99.6
230	343	94.1	>99.9	99.6	99.8	66.6	>99.9	99.8	>99.9	96.6
231	345	94.7	96.1	99.8	99.8	71.9	>99.9	>99.9	>99.9	97.1
232	345	95.1	99.0	99.9	99.9	72.9	>99.9	>99.9	>99.9	97.3
233	347	95.6	>99.9	99.9	99.9	76.2	>99.9	>99.9	>99.9	97.6
234	351	95.5	99.0	99.9	99.9	75.5	>99.9	>99.9	>99.9	97.5
235	355	97.0	99.7	99.9	>99.9	84.9	>99.9	>99.9	>99.9	98.5
236	359	97.7	>99.9	>99.9	>99.9	88.5	>99.9	>99.9	>99.9	98.8
237	360	97.6	99.5	>99.9	>99.9	87.9	>99.9	>99.9	>99.9	98.7
239	363	97.7	99.6	>99.9	>99.9	88.8	>99.9	>99.9	>99.9	98.8
240	365	98.1	>99.9	>99.9	>99.9	90.7	>99.9	>99.9	>99.9	99.0
241	365	98.8	99.8	>99.9	>99.9	94.2	>99.9	>99.9	>99.9	99.4

Time days	Temp C	Pentane	2,3 Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	Total
242	365	98.6	99.6	>99.9	>99.9	92.9	>99.9	>99.9	>99.9	99.3
243	365	98.5	>99.9	>99.9	>99.9	92.7	>99.9	>99.9	>99.9	99.2
244	365	98.3	99.7	>99.9	>99.9	91.3	>99.9	>99.9	>99.9	99.1
245	365	98.5	99.5	>99.9	>99.9	92.3	>99.9	>99.9	>99.9	99.2
246	365	98.4	99.2	>99.9	>99.9	91.8	>99.9	>99.9	>99.9	99.2
247	365	98.2	99.6	>99.9	>99.9	90.7	>99.9	>99.9	>99.9	99.1
249	365	98.1	>99.9	>99.9	>99.9	89.5	>99.9	>99.9	>99.9	99.0
252	368	98.3	99.6	>99.9	>99.9	90.8	>99.9	>99.9	>99.9	99.1
253	368	98.1	99.6	>99.9	>99.9	89.4	>99.9	>99.9	>99.9	98.9
254	368	98.0	99.6	>99.9	>99.9	89.2	>99.9	>99.9	>99.9	98.9
255	370	98.4	99.5	>99.9	>99.9	91.8	>99.9	>99.9	>99.9	99.2
256	370	98.2	99.6	>99.9	>99.9	90.4	>99.9	>99.9	>99.9	99.0
257	372	98.4	99.7	>99.9	>99.9	92.0	>99.9	>99.9	>99.9	99.2
258	372	98.1	99.5	>99.9	>99.9	90.0	>99.9	>99.9	>99.9	99.0
264	374	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9
265	374	98.5	99.7	>99.9	>99.9	92.5	>99.9	>99.9	>99.9	99.2
266	374	98.5	99.7	>99.9	>99.9	92.4	>99.9	>99.9	>99.9	99.2
267	374	98.3	99.6	>99.9	>99.9	91.2	>99.9	>99.9	>99.9	99.1
268	374	98.2	>99.9	>99.9	>99.9	90.9	>99.9	>99.9	>99.9	99.1
269	374	98.2	99.5	>99.9	>99.9	89.9	>99.9	>99.9	>99.9	99.0
270	376	98.2	99.6	>99.9	>99.9	90.6	>99.9	>99.9	>99.9	99.1
271	377	98.4	99.7	>99.9	>99.9	91.9	>99.9	>99.9	>99.9	99.2
272	377	98.4	99.6	>99.9	>99.9	92.1	>99.9	>99.9	>99.9	99.2
274	377	97.8	99.4	>99.9	>99.9	87.7	>99.9	>99.9	>99.9	98.8
275	377	97.9	99.5	>99.9	>99.9	88.6	>99.9	>99.9	>99.9	98.9
276	379	98.1	99.6	>99.9	>99.9	90.2	>99.9	>99.9	>99.9	99.0
277	381	98.3	99.6	>99.9	>99.9	91.2	>99.9	>99.9	>99.9	99.1
278	381	98.2	99.6	>99.9	>99.9	90.5	>99.9	>99.9	>99.9	99.0
280	383	98.1	99.6	>99.9	>99.9	89.5	>99.9	>99.9	>99.9	99.0
281	385	98.2	99.5	>99.9	>99.9	90.2	>99.9	>99.9	>99.9	99.0
282	385	98.0	99.5	>99.9	>99.9	89.0	>99.9	>99.9	>99.9	98.9
284	387	98.2	99.6	>99.9	>99.9	91.3	>99.9	>99.9	>99.9	99.1
285	387	98.2	99.5	>99.9	>99.9	90.9	>99.9	>99.9	>99.9	99.1
286	389	98.0	99.6	>99.9	>99.9	89.7	>99.9	>99.9	>99.9	99.0
287	391	98.1	99.6	>99.9	>99.9	90.5	>99.9	>99.9	>99.9	99.0
289	393	98.1	99.6	>99.9	>99.9	90.6	>99.9	>99.9	>99.9	99.0
290	393	98.2	99.5	>99.9	>99.9	91.4	>99.9	>99.9	>99.9	99.1
291	395	98.1	99.5	>99.9	>99.9	90.5	>99.9	>99.9	>99.9	99.0
292	395	98.3	99.6	>99.9	>99.9	91.6	>99.9	>99.9	>99.9	99.1
293	395	98.1	99.5	>99.9	>99.9	90.7	>99.9	>99.9	>99.9	99.0
294	397	98.0	99.5	>99.9	>99.9	89.9	>99.9	>99.9	>99.9	99.0
297	400	97.7	99.5	>99.9	>99.9	88.1	>99.9	>99.9	>99.9	98.8

Table A-3. Chlorinated Hydrocarbon Conversion Over CK-302 Catalyst

Time days	Temp C	1,1-dichloro-ethylene	Methylene chloride	1,2-dichloro-ethane	trichloro ethylene	Partial Oxidation Products, ppm 1,1,2-trichloro ethane	Chloro -form	Total Conv.
4	400	>99.9	>99.9	>99.9	>99.9	1.3	0.1	99.7
5	400	>99.9	>99.9	>99.9	>99.9	3.7	0.0	99.2
8	400	>99.9	>99.9	>99.9	>99.9	0.7	0.9	99.7
9	400	>99.9	>99.9	99.9	99.9	0.6	0.5	99.7
10	400	>99.9	>99.9	>99.9	>99.9	0.6	0.4	99.8
11	400	>99.9	>99.9	>99.9	>99.9	0.6	0.4	99.8
12	400	>99.9	>99.9	>99.9	>99.9	0.6	0.0	99.9
13	400	99.9	>99.9	>99.9	>99.9	0.5	0.0	99.8
14	400	99.8	>99.9	>99.9	>99.9	0.6	0.0	99.8
15	400	99.8	>99.9	>99.9	>99.9	0.1	0.0	99.9
16	400	99.8	>99.9	>99.9	>99.9	0.1	0.0	99.9
17	400	99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
18	400	>99.9	>99.9	>99.9	>99.9	0.2	0.0	>99.9
19	400	>99.9	>99.9	>99.9	>99.9	0.1	0.0	>99.9
20	400	99.9	>99.9	>99.9	>99.9	0.1	0.0	>99.9
21	400	>99.9	>99.9	>99.9	>99.9	0.1	0.0	>99.9
22	400	>99.9	>99.9	>99.9	>99.9	0.7	0.0	99.8
23	400	>99.9	>99.9	>99.9	>99.9	0.6	0.0	99.9
24	400	>99.9	>99.9	>99.9	>99.9	0.7	0.0	99.9
25	400	>99.9	>99.9	>99.9	>99.9	0.5	0.0	99.9
26	400	>99.9	>99.9	>99.9	>99.9	0.2	0.0	>99.9
27	400	>99.9	>99.9	>99.9	>99.9	0.4	0.0	99.9
28	400	99.9	>99.9	>99.9	>99.9	0.2	0.0	99.9
29	400	99.9	>99.9	>99.9	>99.9	0.4	0.0	99.9
30	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
31	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
32	400	>99.9	>99.9	>99.9	>99.9	0.2	0.0	>99.9
33	400	>99.9	>99.9	>99.9	>99.9	0.1	0.0	>99.9
34	400	99.9	>99.9	99.6	99.7	0.5	0.0	99.7
36	400	99.5	98.7	99.1	99.2	0.2	0.0	99.3
37	400	99.5	98.3	99.3	99.1	0.7	0.0	99.2
38	400	99.9	>99.9	99.6	99.6	1.0	0.0	99.6
39	400	>99.9	>99.9	99.9	99.8	1.1	0.0	99.7
40	400	>99.9	>99.9	>99.9	99.9	1.0	0.0	99.8
41	400	99.9	>99.9	>99.9	99.9	0.0	0.0	>99.9
42	400	>99.9	>99.9	99.9	99.9	0.9	0.0	99.8
43	400	>99.9	>99.9	99.9	99.9	0.8	0.0	99.8
44	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
48	400	>99.9	>99.9	>99.9	>99.9	0.6	0.0	99.9
49	400	>99.9	>99.9	>99.9	>99.9	0.8	0.0	99.8
50	400	>99.9	>99.9	99.7	>99.9	0.4	0.0	99.9
55	400	>99.9	>99.9	99.9	>99.9	0.7	0.0	99.8
56	400	>99.9	>99.9	99.9	>99.9	0.7	0.0	99.8
57	400	99.7	99.7	99.5	99.5	0.9	0.0	99.4
58	400	99.9	>99.9	99.7	99.8	1.7	0.0	99.5
61	400	>99.9	>99.9	99.8	99.9	0.0	0.0	99.9
62	400	>99.9	>99.9	99.9	>99.9	0.7	0.0	99.8
63	400	>99.9	>99.9	99.8	99.9	1.1	0.0	99.7
64	400	>99.9	>99.9	99.6	99.7	1.3	0.0	99.6
65	400	>99.9	>99.9	99.8	99.9	1.4	0.0	99.6
66	400	>99.9	>99.9	99.8	99.9	1.4	0.0	99.6
67	400	>99.9	>99.9	99.9	>99.9	1.4	0.0	99.7
69	400	>99.9	>99.9	99.9	>99.9	0.0	0.0	>99.9
70	400	>99.9	>99.9	99.7	99.9	0.0	0.0	99.9
75	400	>99.9	>99.9	99.5	99.9	1.3	0.0	99.6
76	400	>99.9	>99.9	99.6	99.9	1.1	0.0	99.7
77	400	>99.9	>99.9	99.6	99.9	1.5	0.0	99.6
78	400	>99.9	>99.9	99.5	99.8	1.4	0.0	99.6
79	400	>99.9	>99.9	99.7	99.9	1.9	0.0	99.5
80	400	>99.9	>99.9	99.9	99.9	1.3	0.0	99.7
81	400	>99.9	>99.9	99.9	>99.9	1.3	0.0	99.7
82	400	>99.9	>99.9	99.8	99.9	1.1	0.0	99.7
83	400	>99.9	>99.9	99.8	99.9	1.4	0.0	99.6
84	400	>99.9	>99.9	99.7	>99.9	1.7	0.0	99.6

Time days	Temp C	1,1-dichloro-ethylene	Methylene chloride	1,2-dichloro-ethane	trichloro ethylene	Partial Oxidation Products, ppm 1,1,2-trichloro ethane	Chloro -form	Total Conv.
85	400	>99.9	>99.9	99.8	>99.9	1.4	0.0	99.7
86	400	>99.9	>99.9	99.8	>99.9	1.4	0.0	99.7
87	400	>99.9	>99.9	99.8	>99.9	1.7	0.0	99.6
88	400	>99.9	>99.9	>99.9	>99.9	1.5	0.0	99.7
89	400	>99.9	>99.9	>99.9	>99.9	0.9	0.0	99.8
90	400	>99.9	>99.9	99.7	>99.9	1.1	0.0	99.7
91	400	>99.9	>99.9	99.6	>99.9	1.1	0.0	99.7
92	400	>99.9	>99.9	98.3	>99.9	1.3	0.0	99.3
93	400	>99.9	>99.9	99.2	99.9	1.0	0.0	99.6
94	400	>99.9	>99.9	99.5	>99.9	1.0	0.0	99.7
96	400	99.9	>99.9	99.3	99.7	0.7	0.0	99.6
97	400	99.9	>99.9	99.3	99.7	0.7	0.0	99.6
98	400	>99.9	>99.9	99.6	99.8	0.9	0.0	99.6
99	400	>99.9	>99.9	99.8	99.9	1.1	0.0	99.7
100	400	>99.9	>99.9	99.5	99.9	1.1	0.0	99.6
101	400	>99.9	>99.9	99.6	99.9	0.9	0.0	99.7
102	400	>99.9	>99.9	99.4	99.9	0.8	0.0	99.6
103	400	99.9	99.8	99.1	99.5	1.1	0.0	99.4
104	400	>99.9	>99.9	99.4	99.9	1.1	0.0	99.6
105	400	>99.9	>99.9	99.5	99.9	0.9	0.0	99.7
106	400	>99.9	>99.9	99.9	>99.9	0.9	0.0	99.8
107	400	>99.9	>99.9	99.9	>99.9	0.8	0.0	99.8
108	400	>99.9	>99.9	99.9	>99.9	0.9	0.0	99.8
109	400	>99.9	>99.9	99.9	>99.9	1.1	0.0	99.7
114	400	>99.9	>99.9	99.8	>99.9	1.0	0.0	99.7
115	400	>99.9	>99.9	99.8	>99.9	1.2	0.0	99.7
116	400	>99.9	>99.9	99.8	>99.9	0.0	0.0	>99.9
119	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
120	400	>99.9	>99.9	99.9	>99.9	0.0	0.0	>99.9
121	400	>99.9	>99.9	99.9	>99.9	1.2	0.0	99.7
122	400	>99.9	>99.9	99.8	>99.9	1.6	0.0	99.6
123	400	>99.9	>99.9	99.9	>99.9	1.5	0.0	99.7
124	400	>99.9	>99.9	>99.9	>99.9	1.1	0.0	99.8
125	400	>99.9	>99.9	>99.9	>99.9	1.3	0.0	99.7
127	400	>99.9	>99.9	98.9	>99.9	0.7	0.0	99.6
128	400	>99.9	>99.9	99.9	>99.9	1.5	0.0	99.6
129	400	>99.9	>99.9	>99.9	>99.9	1.4	0.0	99.7
130	400	>99.9	>99.9	>99.9	>99.9	1.4	0.0	99.7
131	400	>99.9	>99.9	99.7	>99.9	1.6	0.0	99.6
132	400	>99.9	>99.9	99.9	>99.9	0.9	0.0	99.8
133	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
134	400	>99.9	>99.9	>99.9	>99.9	1.0	0.0	99.8
135	400	>99.9	>99.9	>99.9	>99.9	0.9	0.0	99.8
136	400	>99.9	>99.9	>99.9	>99.9	0.4	0.0	99.9
137	400	>99.9	>99.9	>99.9	>99.9	0.4	0.0	99.9
138	400	>99.9	>99.9	>99.9	>99.9	0.3	0.0	99.9
139	400	>99.9	>99.9	>99.9	99.9	0.9	0.0	99.8
140	400	>99.9	>99.9	>99.9	99.9	1.0	0.0	99.8
141	400	>99.9	>99.9	>99.9	>99.9	1.1	0.0	99.8
143	400	>99.9	>99.9	>99.9	>99.9	1.1	0.0	99.8
144	400	>99.9	>99.9	>99.9	>99.9	0.9	0.0	99.8
146	400	>99.9	>99.9	>99.9	>99.9	0.9	0.0	99.8
147	400	>99.9	>99.9	>99.9	>99.9	1.3	0.0	99.7
148	400	>99.9	>99.9	>99.9	>99.9	0.6	0.0	99.9
149	400	>99.9	>99.9	>99.9	>99.9	0.3	0.0	99.9
150	400	>99.9	>99.9	>99.9	>99.9	0.7	0.0	99.8
152	400	>99.9	>99.9	>99.9	>99.9	0.5	0.0	99.9
153	400	>99.9	>99.9	99.9	>99.9	0.6	0.0	99.9
154	400	>99.9	>99.9	99.9	>99.9	1.4	0.7	99.6
157	400	>99.9	>99.9	>99.9	>99.9	1.1	0.0	99.8
158	400	>99.9	>99.9	99.9	>99.9	1.1	0.6	99.7
159	400	>99.9	>99.9	99.9	>99.9	0.9	0.6	99.7
160	400	>99.9	>99.9	>99.9	>99.9	1.2	0.6	99.7
161	400	>99.9	>99.9	99.9	>99.9	1.0	0.4	99.7

Table A-3 (continued)

Time days	Temp C	1,1-dichloro-ethylene	Methylene chloride	1,2-dichloro-ethane	trichloro ethylene	Partial Oxidation Products, ppm 1,1,2-trichloro ethane	Chloro-form	Total Conv.
162	400	>99.9	>99.9	99.9	>99.9	1.0	0.6	99.7
163	400	>99.9	>99.9	99.9	>99.9	0.8	0.6	99.7
164	400	>99.9	>99.9	99.9	>99.9	0.7	0.5	99.8
165	400	>99.9	>99.9	>99.9	>99.9	1.2	0.5	99.7
166	400	>99.9	>99.9	99.9	>99.9	0.9	1.0	99.7
167	400	>99.9	>99.9	99.8	>99.9	1.7	1.1	99.5
168	400	>99.9	>99.9	99.9	>99.9	1.8	0.8	99.5
169	400	>99.9	>99.9	99.8	>99.9	1.6	1.0	99.5
170	400	>99.9	>99.9	>99.9	>99.9	1.6	0.9	99.6
171	400	>99.9	>99.9	99.9	>99.9	1.2	0.4	99.7
172	400	>99.9	>99.9	99.8	>99.9	1.3	0.7	99.6
173	400	>99.9	>99.9	99.9	>99.9	1.3	0.7	99.6
174	400	>99.9	>99.9	99.8	>99.9	1.5	0.9	99.5
175	400	>99.9	>99.9	99.8	>99.9	1.3	0.8	99.6
176	400	>99.9	>99.9	99.7	>99.9	1.3	1.0	99.5
177	400	>99.9	>99.9	99.8	>99.9	1.1	0.0	99.7
178	400	>99.9	>99.9	99.8	>99.9	1.4	0.7	99.6
179	400	>99.9	>99.9	>99.9	>99.9	0.8	0.5	99.8
180	400	>99.9	>99.9	99.6	>99.9	1.2	1.0	99.5
181	400	>99.9	>99.9	99.7	>99.9	1.0	0.6	99.7
182	400	>99.9	>99.9	99.8	>99.9	1.0	0.7	99.6
183	400	>99.9	>99.9	99.8	>99.9	1.0	0.5	99.7
184	400	>99.9	>99.9	99.2	>99.9	0.9	0.0	99.6
185	400	>99.9	>99.9	>99.9	99.7	0.5	0.0	99.8
187	400	>99.9	>99.9	>99.9	>99.9	0.3	0.0	99.9
188	400	>99.9	>99.9	>99.9	>99.9	0.3	0.0	99.9
189	400	>99.9	>99.9	99.6	>99.9	0.6	0.0	99.8
190	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
191	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
192	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
203	400	>99.9	>99.9	>99.9	>99.9	1.0	0.0	99.8
204	400	>99.9	>99.9	>99.9	>99.9	0.7	0.0	99.9
205	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	99.9
206	400	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
207	400	>99.9	>99.9	99.7	>99.9	0.9	1.5	99.6
209	400	>99.9	>99.9	98.9	>99.9	0.8	0.0	99.6
210	400	>99.9	>99.9	95.6	99.9	0.7	2.5	95.5
211	400	>99.9	>99.9	97.5	99.9	1.1	0.8	99.1
212	400	>99.9	>99.9	96.1	>99.9	0.9	0.8	98.8
213	400	>99.9	>99.9	97.8	>99.9	1.1	0.3	99.2
215	400	>99.9	>99.9	92.0	99.9	0.3	0.9	98.0
216	400	>99.9	99.4	83.8	99.9	0.2	2.7	95.9
217	400	>99.9	99.2	85.1	99.9	0.2	2.5	96.2
218	400	>99.9	>99.9	97.8	99.9	1.0	0.5	99.2
219	400	>99.9	99.5	89.1	>99.9	0.0	1.7	97.3
220	400	>99.9	>99.9	95.8	99.9	0.2	0.4	98.9
222	400	>99.9	>99.9	99.2	99.9	1.4	0.0	99.5
224	400	>99.9	>99.9	98.6	99.9	1.0	0.0	99.4
225	400	>99.9	>99.9	>99.9	99.9	1.8	0.0	99.6
226	400	>99.9	>99.9	99.2	99.9	1.3	0.0	99.5
229	400	>99.9	>99.9	99.0	99.9	1.0	0.2	99.5
230	400	>99.9	98.4	99.3	>99.9	0.7	0.8	99.4
231	400	>99.9	>99.9	>99.9	>99.9	3.8	0.0	99.1
232	400	>99.9	97.6	>99.9	>99.9	3.9	0.3	99.0
233	400	>99.9	>99.9	99.9	>99.9	3.7	0.0	99.2
234	400	>99.9	99.8	99.9	>99.9	0.0	0.3	99.9
235	400	>99.9	99.8	>99.9	>99.9	3.8	0.2	99.1
236	400	>99.9	>99.9	>99.9	>99.9	3.4	0.3	99.2
237	400	>99.9	99.8	>99.9	>99.9	3.9	0.3	99.1
238	400	>99.9	99.8	>99.9	>99.9	3.7	0.3	99.2
240	400	>99.9	>99.9	>99.9	>99.9	3.8	0.0	99.2
241	400	>99.9	>99.9	>99.9	>99.9	3.3	0.0	99.3
242	400	>99.9	>99.9	>99.9	>99.9	3.5	0.0	99.2
243	400	>99.9	>99.9	>99.9	>99.9	3.4	0.3	99.2

74

Table A-3 (continued)

Time days	Temp C	1,1-dichloro-ethylene	Methylene chloride	1,2-dichloro-ethane	trichloro ethylene	Partial Oxidation Products, ppm 1,1,2-trichloro ethane	Chloro -form	Total Conv.
244	400	>99.9	>99.9	>99.9	>99.9	3.7	0.4	99.2
245	400	>99.9	>99.9	>99.9	>99.9	3.4	0.4	99.2
246	400	>99.9	>99.9	>99.9	>99.9	3.5	0.5	99.2
247	400	>99.9	>99.9	>99.9	>99.9	3.7	0.4	99.2

Table A-4. "Mixed-Stream" Conversion Over CK-302 Catalyst in the Fixed-Bed Reactor

Time days	Temp C	Pentane	2,3-Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	TCE	Concentration of Partial Oxidation Products 1,1,2 tri- chloroethane	chloro- form	Total
1	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9	N.D.	N.D.	>99.9
4	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9	N.D.	N.D.	>99.9
5	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.6	2.1	N.D.	99.8
6	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.6	2.0	N.D.	99.8
7	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.6	1.9	N.D.	99.8
8	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.7	2.1	N.D.	99.8
9	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9	N.D.	N.D.	>99.9
10	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	99.8	6.9	N.D.	99.5
11	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.8	6.4	N.D.	99.6
12	350	>99.9	>99.9	>99.9	>99.9	99.9	99.9	99.8	>99.9	99.7	7.0	N.D.	99.4
13	350	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	99.9	>99.9	99.6	6.7	N.D.	99.5
14	350	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	99.9	>99.9	99.6	6.7	N.D.	99.5
15	350	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	99.5	7.6	N.D.	99.4
16	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	99.5	6.4	N.D.	99.5
17	350	>99.9	>99.9	>99.9	>99.9	99.8	>99.9	>99.9	>99.9	99.6	6.3	0.2	99.5
18	350	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	99.9	>99.9	99.5	6.5	0.2	99.5
19	350	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	99.9	>99.9	99.4	6.6	0.5	99.5
20	350	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	99.9	>99.9	99.6	5.4	0.4	99.6
21	350	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	99.7	5.1	0.3	99.6
22	350	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	99.7	4.8	N.D.	99.6
23	350	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	99.7	4.3	0.4	99.7
24	350	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	99.8	4.4	0.4	99.6
25	350	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	99.8	3.7	0.1	99.7
26	350	>99.9	>99.9	>99.9	>99.9	99.4	>99.9	>99.9	>99.9	>99.9	4.2	0.4	99.7
27	350	>99.9	>99.9	>99.9	>99.9	99.5	>99.9	>99.9	>99.9	99.7	3.6	0.4	99.7
28	350	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	99.7	4.5	0.4	99.6
29	350	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	99.7	4.0	0.4	99.7
30	350	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	99.7	4.9	N.D.	99.6
31	350	>99.9	99.6	>99.9	>99.9	98.9	>99.9	99.9	>99.9	98.3	2.4	0.5	99.7
34	350	99.9	>99.9	>99.9	>99.9	98.9	>99.9	>99.9	>99.9	99.3	0.8	0.4	99.8
35	350	99.9	>99.9	>99.9	>99.9	99.3	>99.9	>99.9	>99.9	>99.9	1.8	0.3	99.8
36	350	>99.9	>99.9	>99.9	>99.9	99.3	>99.9	>99.9	>99.9	99.6	2.3	0.4	99.8
37	350	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	99.7	3.9	0.3	99.7
38	350	99.9	>99.9	>99.9	>99.9	99.2	>99.9	>99.9	>99.9	99.6	0.5	0.4	99.9
49	350	99.9	>99.9	>99.9	>99.9	99.0	>99.9	>99.9	>99.9	99.8	1.1	0.4	99.8
50	350	99.9	>99.9	>99.9	>99.9	99.2	>99.9	>99.9	99.4	>99.9	2.3	N.D.	99.8
51	350	99.9	>99.9	>99.9	>99.9	99.2	>99.9	>99.9	>99.9	99.8	1.9	N.D.	99.8
52	350	99.8	>99.9	>99.9	>99.9	98.6	>99.9	>99.9	>99.9	99.7	1.0	N.D.	99.8
53	350	>99.9	>99.9	>99.9	>99.9	99.6	>99.9	>99.9	>99.9	>99.9	0.5	N.D.	99.9
54	350	99.0	>99.9	98.7	99.3	97.4	>99.9	>99.9	>99.9	99.8	0.8	N.D.	99.2
56	350	>99.9	>99.9	>99.9	>99.9	>99.9	99.4	99.5	99.5	>99.9	N.D.	0.5	99.9
57	350	99.9	>99.9	99.8	99.8	99.0	>99.9	>99.9	>99.9	99.7	1.5	N.D.	99.7
58	350	99.9	>99.9	99.8	99.9	98.9	99.8	99.8	99.6	99.9	1.1	0.1	99.7
59	350	99.9	>99.9	>99.9	>99.9	99.2	99.8	99.8	99.8	99.8	2.8	0.2	99.7
60	350	99.9	>99.9	>99.9	>99.9	99.3	>99.9	>99.9	>99.9	>99.9	0.8	N.D.	99.9
62	350	99.9	>99.9	>99.9	>99.9	98.9	>99.9	>99.9	>99.9	>99.9	0.5	N.D.	99.9
63	350	99.7	>99.9	>99.9	>99.9	97.7	99.9	99.9	>99.9	>99.9	1.0	0.9	99.7
64	350	99.8	>99.9	>99.9	>99.9	98.3	>99.9	>99.9	>99.9	99.8	0.8	0.3	99.8
65	350	99.9	>99.9	>99.9	>99.9	99.5	>99.9	>99.9	>99.9	>99.9	0.5	N.D.	99.9
66	350	99.8	>99.9	>99.9	>99.9	98.2	>99.9	>99.9	>99.9	99.9	0.2	N.D.	99.8
67	350	99.8	>99.9	>99.9	>99.9	97.7	>99.9	>99.9	>99.9	99.8	N.D.	0.3	99.8
69	350	99.9	>99.9	>99.9	>99.9	98.4	>99.9	>99.9	>99.9	99.7	1.9	0.4	99.7
71	350	99.8	>99.9	>99.9	>99.9	98.7	>99.9	>99.9	>99.9	99.8	1.7	N.D.	99.8
72	350	99.9	>99.9	>99.9	>99.9	98.9	>99.9	>99.9	>99.9	99.8	1.9	0.6	99.7
73	350	99.9	99.6	>99.9	>99.9	99.1	>99.9	>99.9	>99.9	99.9	1.7	0.3	99.8
76	350	99.9	>99.9	>99.9	>99.9	99.0	>99.9	>99.9	>99.9	99.8	1.7	0.5	99.8
77	350	>99.9	>99.9	99.9	>99.9	99.8	99.9	>99.9	99.7	>99.9	5.1	N.D.	99.6
78	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	5.2	N.D.	99.6
79	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	5.2	N.D.	99.6
80	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	5.2	N.D.	99.6
81	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.4	N.D.	99.7
82	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.4	N.D.	99.7
83	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.1	N.D.	99.7

N.D. = not detectable

76

Time days	Temp C	Pentane	2,3-Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	TCE	Concentration of Partial Oxidation Products 1,1,2 tri- chloroethane	chloro- form	Total
84	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.1	N.D.	99.7
85	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.6	N.D.	99.7
87	350	>99.9	>99.9	>99.9	>59.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.1	N.D.	99.7
88	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.4	N.D.	99.7
89	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.3	N.D.	99.7
90	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.3	N.D.	99.7
91	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.3	N.D.	99.7
92	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.5	N.D.	99.7
93	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.4	N.D.	99.7
94	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.3	N.D.	99.7
96	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.3	N.D.	99.7
98	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.5	N.D.	99.8
99	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.7	N.D.	99.8
100	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.6	N.D.	99.8
101	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.8	N.D.	99.7
102	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.3	N.D.	99.8
104	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.6	N.D.	99.8
105	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.6	N.D.	99.8
112	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.8	N.D.	99.7
113	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.7	N.D.	99.7
114	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.0	N.D.	99.7
115	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.0	N.D.	99.7
116	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.8	N.D.	99.7
117	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.2	N.D.	99.7
118	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.8	N.D.	99.7
119	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.7	N.D.	99.7
120	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.8	N.D.	99.7
121	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.7	N.D.	99.7
122	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.7	N.D.	99.7
123	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.8	N.D.	99.7
124	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.4	N.D.	99.8
125	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.8	N.D.	99.7
127	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	3.8	N.D.	99.7
128	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.0	N.D.	99.7
129	350	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	>99.9	4.0	N.D.	99.7

N.D. = not detectable

Table A-5 Chlorinated Hydrocarbon Conversion Over ARI Catalyst in Fluid-Bed Reactor

Time days	Temp C	1,1-dichloro-ethylene	Methylene chloride	1,2-dichloro-ethane	trichloro ethylene	Partial Oxidation Products, ppm 1,1,2-trichloro ethane	Chloro -form	Total Conv.
0	350	99.9	97.4	98.9	99.0	N.D.	N.D.	99.3
1	350	99.9	97.5	99.0	98.8	N.D.	N.D.	99.3
2	350	>99.9	97.9	99.0	99.5	N.D.	N.D.	99.5
3	350	99.9	94.1	97.2	97.9	N.D.	N.D.	98.5
4	350	>99.9	97.8	99.1	98.9	N.D.	N.D.	99.4
5	350	>99.9	97.4	98.9	98.9	N.D.	N.D.	99.4
6	350	99.6	96.8	98.5	98.7	N.D.	N.D.	99.0
7	350	>99.9	96.9	98.6	98.6	N.D.	N.D.	99.2
8	350	99.7	97.7	99.1	99.1	N.D.	N.D.	99.3
9	350	99.6	96.2	98.3	98.2	N.D.	N.D.	98.8
10	354	99.7	96.8	98.6	98.7	N.D.	N.D.	99.0
11	354	99.8	97.0	98.6	98.8	N.D.	N.D.	99.1
12	354	99.6	99.3	>99.9	>99.9	N.D.	N.D.	99.8
13	354	99.7	99.3	>99.9	>99.9	N.D.	N.D.	99.9
14	354	99.8	99.5	>99.9	>99.9	N.D.	N.D.	99.9
15	354	99.8	97.7	99.9	>99.9	N.D.	N.D.	99.7
16	354	99.9	97.6	98.9	98.9	N.D.	N.D.	99.3
17	354	99.9	96.1	98.2	98.1	0.1	N.D.	98.9
18	354	99.8	97.3	98.7	98.8	N.D.	N.D.	99.2
20	354	99.9	96.7	98.6	98.6	N.D.	N.D.	99.1
21	354	99.9	96.5	98.1	98.3	N.D.	N.D.	98.9
22	354	99.6	96.5	98.6	98.8	N.D.	N.D.	99.0
23	354	99.9	96.3	98.3	98.6	N.D.	N.D.	99.0
24	354	99.8	96.7	98.4	98.6	N.D.	N.D.	99.0
25	354	99.6	96.2	98.3	98.5	N.D.	N.D.	98.8
26	354	99.8	96.9	98.8	99.0	N.D.	N.D.	99.2
27	354	99.8	98.1	99.4	99.2	N.D.	N.D.	99.5
28	354	99.5	94.7	98.5	98.6	N.D.	N.D.	98.8
32	354	99.9	97.4	98.7	98.8	N.D.	N.D.	99.2
33	354	99.8	96.8	98.5	98.6	N.D.	N.D.	99.1
34	354	>99.9	97.5	98.9	99.1	N.D.	N.D.	99.4
39	354	99.9	97.0	98.6	98.6	0.1	N.D.	99.1
40	354	>99.9	96.8	98.4	98.5	N.D.	N.D.	99.1
41	354	99.7	96.7	98.4	98.5	N.D.	N.D.	98.9
42	357	99.8	96.7	98.3	98.4	N.D.	N.D.	99.0
45	360	>99.9	>99.9	99.2	99.2	N.D.	N.D.	99.6
46	360	>99.9	97.6	98.9	98.9	N.D.	N.D.	99.3
47	360	>99.9	98.4	99.2	99.1	N.D.	N.D.	99.5
48	360	99.9	97.7	99.0	99.1	N.D.	N.D.	99.4
49	360	>99.9	98.1	99.1	99.1	N.D.	N.D.	99.4
50	360	>99.9	98.2	99.2	99.2	N.D.	N.D.	99.5
51	360	>99.9	97.6	98.9	98.9	N.D.	N.D.	99.3
53	360	>99.9	98.4	99.3	99.3	N.D.	N.D.	99.6
54	360	99.5	99.1	98.6	98.6	0.4	N.D.	98.9
59	360	>99.9	98.1	99.1	99.1	N.D.	N.D.	99.5
60	360	99.9	97.8	98.8	98.9	N.D.	N.D.	99.3
61	360	>99.9	98.2	99.3	99.1	0.1	N.D.	99.5
62	360	>99.9	97.8	98.8	99.0	0.2	N.D.	99.3
63	360	>99.9	98.1	99.1	99.1	0.4	N.D.	99.4
64	360	>99.9	98.8	99.5	99.5	0.3	N.D.	99.6
65	360	>99.9	98.5	99.4	99.4	0.3	N.D.	99.6
66	360	>99.9	98.5	99.6	99.5	0.1	N.D.	99.7
67	360	99.9	97.6	98.9	98.8	0.1	N.D.	99.2
68	360	>99.9	97.8	99.1	99.0	N.D.	N.D.	99.4
69	360	99.9	97.6	98.9	98.8	N.D.	N.D.	99.3
70	360	>99.9	99.0	99.4	99.5	0.2	N.D.	99.7
71	360	>99.9	98.2	99.3	99.2	N.D.	N.D.	99.6
72	360	>99.9	98.1	99.2	99.1	N.D.	N.D.	99.5
73	360	99.9	>99.9	98.8	98.9	0.1	N.D.	99.4
74	360	>99.9	>99.9	99.0	99.3	N.D.	N.D.	99.6
75	360	>99.9	97.2	98.6	98.7	N.D.	N.D.	99.2

N.D. = not detectable

Time days	Temp C	1,1-dichloro-ethylene	Methylene chloride	1,2-dichloro-ethane	trichloro ethylene	Partial Oxidation Products, ppm 1,1,2-trichloro ethane	Chloro -form	Total Conv.
76	360	>99.9	98.5	98.8	99.4	N.D.	N.D.	99.5
77	360	>99.9	98.3	98.9	99.5	N.D.	N.D.	99.5
78	360	>99.9	99.1	99.6	99.8	N.D.	N.D.	99.8
79	360	>99.9	98.3	99.2	99.3	N.D.	N.D.	99.6
80	360	99.9	98.0	98.9	98.7	N.D.	N.D.	99.3
81	360	99.9	98.3	99.1	98.9	0.1	N.D.	99.4
82	360	99.9	97.8	98.8	98.8	N.D.	N.D.	99.3
83	360	>99.9	98.7	99.5	99.6	N.D.	N.D.	99.7
84	360	>99.9	98.0	99.1	99.0	N.D.	N.D.	99.4
85	360	99.9	97.4	98.7	98.7	N.D.	N.D.	99.2
86	360	99.9	97.9	99.0	98.9	N.D.	N.D.	99.4
87	360	>99.9	97.8	99.1	99.1	N.D.	N.D.	99.4
88	360	>99.9	98.3	99.3	99.5	0.2	N.D.	99.6
89	360	99.9	97.8	99.1	99.2	N.D.	N.D.	99.4
90	360	99.9	97.0	98.5	98.8	N.D.	N.D.	99.2
91	360	>99.9	98.1	99.3	99.4	N.D.	N.D.	99.6
92	360	99.9	97.9	99.3	99.3	N.D.	N.D.	99.5
93	360	99.9	97.8	99.2	99.3	N.D.	N.D.	99.5
98	360	99.9	97.4	98.9	99.0	N.D.	N.D.	99.4
99	360	>99.9	97.3	99.0	99.2	0.2	N.D.	99.4
102	360	>99.9	>99.9	99.3	99.3	N.D.	N.D.	99.7
103	360	>99.9	>99.9	99.1	99.0	N.D.	N.D.	99.5
104	360	99.9	97.4	98.9	98.8	N.D.	N.D.	99.3
105	360	>99.9	98.5	99.5	99.6	N.D.	N.D.	99.7
106	360	99.9	97.2	98.9	98.9	N.D.	N.D.	99.3
107	360	99.9	96.0	97.9	98.0	N.D.	N.D.	98.8
108	360	99.9	96.8	98.5	98.8	N.D.	N.D.	99.1
109	360	99.9	97.7	99.1	99.1	N.D.	N.D.	99.4
111	360	>99.9	98.8	98.9	93.9	N.D.	N.D.	99.4
112	360	99.9	>99.9	98.2	98.1	N.D.	N.D.	99.1
113	360	>99.9	>99.9	98.0	97.8	N.D.	N.D.	99.0
116	360	99.9	>99.9	98.7	98.5	N.D.	N.D.	99.3
115	350	>99.9	97.6	99.0	98.9	N.D.	N.D.	99.4
116	360	>99.9	98.6	99.4	99.3	N.D.	N.D.	99.6
117	360	>99.9	>99.9	>99.9	>99.9	N.D.	N.D.	>99.9
118	360	>99.9	>99.9	>99.9	99.4	N.D.	N.D.	99.9
119	360	99.9	96.8	98.7	98.5	N.D.	N.D.	99.1
120	360	>99.9	97.4	98.9	98.4	0.1	N.D.	99.2
121	360	>99.9	97.1	98.8	98.2	0.2	N.D.	99.1
122	360	>99.9	97.3	98.9	98.5	0.3	N.D.	99.2
123	360	99.9	99.3	99.8	99.8	N.D.	N.D.	99.8
124	360	99.9	97.2	98.8	98.7	N.D.	N.D.	99.2
125	360	99.9	97.5	99.0	98.9	N.D.	N.D.	99.4
127	360	99.9	97.4	98.8	98.6	N.D.	N.D.	99.2
128	360	>99.9	98.6	99.5	99.5	N.D.	N.D.	99.7
130	360	>99.9	97.6	98.9	98.7	N.D.	N.D.	99.3
131	360	99.9	97.1	98.6	98.3	N.D.	N.D.	99.1
132	360	99.9	97.0	98.6	98.4	N.D.	N.D.	99.1
133	360	>99.9	97.9	99.1	99.0	N.D.	N.D.	99.4
134	360	>99.9	98.0	99.3	99.3	N.D.	N.D.	99.6
136	360	99.9	97.3	98.8	98.7	N.D.	N.D.	99.2
137	360	>99.9	98.1	99.2	99.2	0.3	N.D.	99.5
140	360	99.9	97.0	98.7	98.5	0.2	0.5	99.1
143	360	>99.9	98.1	99.2	99.1	0.3	0.3	99.4
144	360	99.9	97.4	98.7	98.8	0.2	0.6	99.1
145	360	99.9	96.1	98.0	97.8	0.2	0.6	98.6
146	361	>99.9	97.3	98.7	98.6	0.2	0.7	99.1
147	361	>99.9	97.8	99.1	98.9	0.3	0.5	99.3
148	361	99.9	96.3	98.3	97.9	0.5	0.5	98.7
149	361	>99.9	97.6	99.0	98.9	0.2	0.5	99.3
150	361	>99.9	97.4	99.0	99.3	0.3	0.5	99.3

N.D. = not detectable

Table A-5 (continued)

Time days	Temp C	1,1-dichloro-ethylene	Methylene chloride	1,2-dichloro-ethane	trichloro ethylene	Partial Oxidation Products, ppm		Total Conv.
						1,1,2-trichloro ethane	Chloro-form	
151	361	>99.9	97.8	99.1	98.9	0.2	0.6	99.3
152	361	>99.9	98.3	99.0	98.9	0.4	0.9	99.2
153	361	>99.9	97.7	99.1	98.8	0.3	0.7	99.2
154	361	99.9	97.3	98.9	98.6	0.5	0.5	99.1
155	361	99.9	97.4	98.7	98.5	0.5	0.8	99.0
156	361	>99.9	97.8	99.1	98.8	0.4	0.6	99.2
157	361	>99.9	98.1	99.2	99.1	0.3	0.5	99.3
158	361	99.9	97.3	98.7	98.4	0.3	0.8	99.0
159	361	>99.9	97.9	99.3	99.0	0.4	0.7	99.3
160	361	99.9	96.8	98.6	98.2	0.4	0.6	98.9
161	361	>99.9	98.1	99.2	99.0	0.7	0.5	99.2
162	361	>99.9	97.9	99.0	98.8	0.6	0.6	99.1
163	361	>99.9	98.2	99.2	99.2	0.5	0.5	99.3
164	361	>99.9	97.8	98.8	98.7	0.6	0.6	99.1
165	361	>99.9	97.9	99.0	99.5	0.5	0.7	99.3
166	361	>99.9	97.2	98.7	98.4	0.5	0.5	99.0
167	361	>99.9	97.6	98.9	98.8	0.8	0.6	99.1
168	361	99.9	>99.9	98.6	98.3	0.5	0.5	99.1
169	361	99.9	97.6	99.1	98.7	0.5	0.4	99.2
170	361	>99.9	97.2	98.7	98.5	0.5	0.5	99.0
171	361	99.9	97.4	98.6	98.2	0.6	0.6	98.9
173	361	>99.9	98.2	99.1	99.0	0.9	N.D.	99.3
174	361	>99.9	98.4	99.0	99.2	1.2	0.2	99.2
175	361	>99.9	98.2	99.1	98.9	0.5	0.5	99.3
176	361	>99.9	98.1	99.2	99.1	0.6	0.3	99.3
177	361	>99.9	>99.9	>99.9	>99.9	N.D.	N.D.	>99.9
188	361	>99.9	98.0	98.9	98.9	0.7	0.6	99.2
189	361	>99.9	97.8	98.8	99.1	1.5	N.D.	99.1
190	361	>99.9	97.9	98.8	>99.9	N.D.	N.D.	99.6
191	361	>99.9	98.3	99.0	99.5	N.D.	N.D.	99.6
192	361	>99.9	98.0	>99.9	>99.9	N.D.	N.D.	99.9
193	361	>99.9	>99.9	98.4	99.9	2.5	9.0	98.1
195	361	>99.9	98.4	99.0	99.4	2.1	0.6	99.0
196	361	>99.9	>99.9	98.0	97.9	1.1	1.3	98.6

Time days	Temp C	1,1dichloro-ethylene	methylene chloride	1,2dichloro-ethane	trichloro-ethylene	1,1,2trichloro ethane	Chloroform	Total
197	361	>99.9	>99.9	99	99.7	3.4	1.6	98.8
198	361	>99.9	97.1	98.6	98.6	0.9	0.7	98.9
199	361	>99.9	97.5	98.9	98.8	0.8	0.2	99.1
201	361	>99.9	>99.9	99.7	>99.9	2.4	0.5	99.7
202	361	>99.9	>99.9	99.6	>99.9	2.6	0.6	99.6
203	361	>99.9	>99.9	99.7	>99.9	1.9	0.3	99.8
204	361	>99.9	>99.9	99.7	>99.9	1.9	0.3	99.7
205	361	>99.9	>99.9	99.6	>99.9	2.2	0.3	99.7
206	361	>99.9	>99.9	89.5	>99.9	2.5	0.4	98.7
209	361	>99.9	99.4	99.6	99.8	1.2	0.2	99.7
211	361	>99.9	>99.9	99.7	>99.9	2.8	0.0	99.7
212	361	>99.9	99.9	99.7	>99.9	3.1	0.1	99.
213	361	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
216	362	>99.9	98.7	99.4	99.3	0.0	0.0	99.6
217	362	>99.9	98.8	99.6	99.4	0.2	0.0	99.7
218	362	>99.9	98.2	99.2	99.1	0.2	0.2	89.4
219	362	>99.9	98.7	99.8	99.4	0.1	0.2	99.7
220	362	>99.9	98.8	99.6	99.6	0.0	0.3	89.7
221	362	>99.9	98.4	99.1	>99.9	0.0	0.2	99.7
222	363	>99.9	98.7	99.5	99.4	0.1	0.3	99.6
223	363	>99.9	98.2	99.4	99.1	0.0	0.3	99.5
224	364	>99.9	98.5	99.4	99.3	0.1	0.2	99.6
229	367	>99.9	98.6	99.5	99.3	0.2	0.3	99.6
230	367	>99.9	98.5	99.4	99.2	0.3	0.3	99.5
231	368	>99.9	98.4	99.3	99.1	0.2	0.3	39.5
232	368	>99.9	98.4	99.3	99.2	0.2	0.3	99.5
233	368	>99.9	98.9	99.6	99.5	0.2	0.2	99.7
238	370	>99.9	99.0	99.6	99.5	0.4	0.5	89.7

Table A-6. "Mixed-Stream" Conversion Over ARI Catalyst in the Fluid-Bed Reactor

Time days	Temp C	Pentane	2,3-Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	TCE	1,1,2 tri-chloroethane	Total
1	350	98.1	98.0	99.2	99.4	71.9	99.8	99.9	>99.9	90.4	N.D.	97.4
2	350	99.4	98.8	99.8	99.9	82.7	99.5	99.3	99.0	94.6	N.D.	98.5
3	350	94.4	94.3	96.6	97.1	60.0	99.0	99.5	97.8	85.1	N.D.	94.5
4	350	96.1	95.8	98.0	98.5	63.9	99.7	99.8	98.8	86.8	N.D.	95.9
5	385	99.7	99.6	>99.9	>99.9	92.1	>99.9	99.9	>99.9	96.7	N.D.	99.4
6	385	99.9	>99.9	>99.9	>99.9	95.5	>99.9	99.9	>99.9	98.0	N.D.	99.6
7	385	99.3	99.3	99.8	99.9	86.2	>99.9	99.9	>99.9	95.3	N.D.	98.9
8	388	>99.9	>99.9	>99.9	>99.9	96.1	>99.9	>99.9	>99.9	98.2	N.D.	99.7
9	388	99.9	>99.9	>99.9	>99.9	96.7	>99.9	99.9	>99.9	98.4	N.D.	99.7
10	388	>99.9	>99.9	>99.9	>99.9	96.7	>99.9	>99.9	>99.9	98.5	N.D.	99.7
11	388	98.8	98.8	99.6	99.8	82.1	>99.9	>99.9	>99.9	94.4	N.D.	98.5
12	388	99.9	>99.9	>99.9	>99.9	95.4	>99.9	>99.9	>99.9	98.1	N.D.	99.7
13	388	>99.9	>99.9	>99.9	>99.9	97.6	>99.9	>99.9	>99.9	98.9	N.D.	99.8
14	388	99.9	>99.9	>99.9	>99.9	95.6	>99.9	>99.9	>99.9	98.2	N.D.	99.7
15	388	>99.9	>99.9	>99.9	>99.9	97.2	>99.9	>99.9	>99.9	98.7	N.D.	99.8
16	388	99.7	>99.9	99.7	99.7	96.5	99.7	99.7	>99.9	98.6	N.D.	99.5
17	388	99.9	>99.9	99.9	99.9	98.0	99.6	99.7	>99.9	99.0	N.D.	99.7
18	388	99.5	99.4	99.6	99.7	89.6	98.7	98.4	99.0	96.4	N.D.	98.7
19	388	98.8	98.9	99.6	99.7	80.7	98.6	98.4	>99.9	93.8	N.D.	98.0
20	388	99.1	99.0	99.8	99.9	80.6	99.2	99.1	99.5	93.5	N.D.	98.2
21	390	99.9	>99.9	>99.9	>99.9	95.4	99.7	99.6	99.7	98.1	N.D.	99.5
22	390	99.2	98.8	99.8	99.9	83.8	99.6	99.5	99.8	94.4	N.D.	98.6
23	392	99.8	99.7	>99.9	>99.9	92.4	99.7	99.6	>99.9	97.1	N.D.	99.3
24	392	99.8	>99.9	>99.9	>99.9	93.5	99.8	99.8	>99.9	97.3	N.D.	99.5
25	392	99.5	99.6	>99.9	>99.9	87.3	99.7	99.7	99.9	95.3	N.D.	99.0
26	392	99.6	99.4	>99.9	>99.9	87.7	99.9	99.8	>99.9	95.7	N.D.	99.0
27	392	>99.9	>99.9	>99.9	>99.9	99.2	99.8	99.8	>99.9	99.2	N.D.	99.9
28	392	99.6	99.4	>99.9	>99.9	88.4	>99.9	99.9	>99.9	96.0	N.D.	99.1
29	392	99.3	99.3	99.8	99.9	85.4	99.5	99.4	99.7	94.7	N.D.	98.7
30	394	>99.9	>99.9	>99.9	>99.9	97.6	>99.9	99.8	>99.9	98.5	N.D.	99.8
31	394	99.7	99.7	>99.9	>99.9	89.7	>99.9	99.8	>99.9	96.0	N.D.	99.2
32	394	99.5	99.5	>99.9	>99.9	85.5	>99.9	99.9	>99.9	94.8	N.D.	98.9
33	395	99.5	>99.9	>99.9	>99.9	85.9	>99.9	>99.9	>99.9	94.9	N.D.	98.9
34	397	>99.9	>99.9	>99.9	>99.9	93.0	>99.9	99.9	>99.9	98.9	N.D.	99.8
35	397	99.8	>99.9	>99.9	>99.9	91.6	>99.9	99.9	>99.9	96.9	N.D.	99.6
40	399	99.9	>99.9	>99.9	>99.9	92.9	>99.9	99.9	>99.9	97.1	N.D.	99.5
41	399	99.6	99.4	>99.9	>99.9	88.6	>99.9	99.9	>99.9	95.9	N.D.	99.1
44	400	99.8	>99.9	>99.9	>99.9	91.9	>99.9	99.9	>99.9	97.2	N.D.	99.4
45	400	99.4	99.3	99.9	>99.9	84.9	>99.9	>99.9	>99.9	95.1	N.D.	98.8
45	401	99.3	99.2	99.9	>99.9	83.7	>99.9	99.9	>99.9	94.7	N.D.	98.7
47	401	99.9	>99.9	>99.9	>99.9	93.8	>99.9	99.9	>99.9	97.5	N.D.	99.5
48	401	>99.9	>99.9	>99.9	>99.9	96.1	>99.9	>99.9	>99.9	98.0	N.D.	99.7
49	401	99.3	99.3	95.9	>99.9	83.1	>99.9	99.9	>99.9	93.9	N.D.	98.7
50	402	99.8	99.7	>99.9	>99.9	92.1	>99.9	>99.9	>99.9	97.9	N.D.	99.4
51	402	99.9	>99.9	>99.9	>99.9	94.6	>99.9	99.9	>99.9	97.9	N.D.	99.6
53	402	99.6	99.4	99.9	99.9	91.9	99.6	99.4	99.2	97.3	N.D.	99.2
54	403	99.6	99.6	>99.9	>99.9	88.7	99.7	99.8	>99.9	95.9	N.D.	99.1
55	403	99.9	>99.9	>99.9	>99.9	94.7	99.9	99.9	>99.9	97.6	N.D.	99.6
56	403	99.7	99.5	>99.9	>99.9	93.5	99.7	99.7	>99.9	97.6	N.D.	99.5
57	403	98.8	99.0	99.8	99.9	77.5	>99.9	99.8	>99.9	93.0	N.D.	98.2
58	403	>99.9	>99.9	>99.9	>99.9	97.3	>99.9	99.7	>99.9	98.6	N.D.	99.7
60	403	>99.9	>99.9	>99.9	>99.9	95.1	99.7	>99.9	>99.9	97.9	N.D.	99.6
61	403	99.7	>99.9	>99.9	>99.9	91.1	>99.9	>99.9	>99.9	96.7	N.D.	99.3
62	403	99.4	99.3	99.9	>99.9	85.5	>99.9	>99.9	>99.9	94.9	N.D.	98.9
63	403	99.7	99.7	>99.9	>99.9	89.0	>99.9	99.8	>99.9	95.9	N.D.	99.2
64	403	99.6	99.6	>99.9	>99.9	88.2	99.9	99.9	>99.9	96.1	N.D.	99.1
65	403	99.6	99.6	>99.9	>99.9	87.5	>99.9	99.8	>99.9	95.6	N.D.	99.0
66	403	99.5	99.5	99.9	>99.9	86.0	>99.9	99.9	>99.9	94.9	N.D.	98.9
67	404	98.4	99.6	99.6	99.8	75.4	>99.9	>99.9	>99.9	91.6	N.D.	97.9
69	404	99.1	98.9	99.7	99.9	81.1	>99.9	99.9	>99.9	93.5	N.D.	98.5
70	404	99.1	99.2	99.8	99.9	80.9	>99.9	99.9	>99.9	93.5	N.D.	98.5
72	405	99.6	99.6	>99.9	>99.9	88.0	>99.9	>99.9	>99.9	95.7	N.D.	99.1

N.D. = not detectable

82

Table A-6 (continued)

Time days	Temp C	Pentane	2,3-Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	TCE	1,1,2 tri-chloroethane	Total
73	405	99.3	99.4	99.9	>99.9	84.6	>99.9	>99.9	>99.9	94.6	N.D.	98.8
74	406	99.5	99.3	99.9	>99.9	87.5	>99.9	99.9	>99.9	95.4	N.D.	99.0
75	406	99.9	>99.9	>99.9	>99.9	94.6	>99.9	>99.9	>99.9	97.8	N.D.	99.6
76	406	99.8	>99.9	>99.9	>99.9	91.8	>99.9	>99.9	>99.9	96.8	N.D.	99.4
78	406	99.6	99.6	>99.9	>99.9	87.5	>99.9	99.8	>99.9	95.6	N.D.	99.0
79	406	99.5	99.5	99.9	>99.9	86.0	>99.9	99.9	>99.9	94.9	N.D.	98.9
82	406	99.9	>99.9	>99.9	>99.9	94.3	>99.9	>99.9	>99.9	97.4	N.D.	99.6
85	406	>99.9	>99.9	>99.9	>99.9	95.9	>99.9	>99.9	>99.9	97.8	N.D.	99.7
86	406	99.5	99.3	>99.9	>99.9	87.4	>99.9	>99.9	>99.9	94.6	N.D.	99.0
	406	99.9	>99.9	>99.9	>99.9	94.2	>99.9	>99.9	>99.9	97.2	N.D.	99.6
	406	99.9	>99.9	>99.9	>99.9	94.6	>99.9	>99.9	>99.9	97.3	N.D.	99.6
89	406	99.8	>99.9	>99.9	>99.9	90.4	>99.9	>99.9	>99.9	95.4	N.D.	99.3
90	406	95.8	>99.9	>99.9	>99.9	91.3	>99.9	>99.9	>99.9	96.0	N.D.	99.3
91	406	95.9	>99.9	>99.9	>99.9	92.4	>99.9	>99.9	>99.9	96.2	N.D.	99.4
92	406	99.7	99.7	>99.9	>99.9	88.3	>99.9	>99.9	>99.9	94.8	0.2	99.1
93	406	99.7	>99.9	>99.9	>99.9	90.4	>99.9	>99.	>99.9	97.1	N.D.	99.3
94	406	99.9	99.7	99.9	99.9	98.4	99.6	99.5	99.6	98.7	0.6	99.6
95	406	99.7	99.2	99.8	>99.9	95.2	>99.9	>99.9	>99.9	97.9	N.D.	99.6
96	406	99.5	98.9	99.8	99.9	90.4	>99.9	>99.9	>99.9	96.0	N.D.	99.1
97	406	99.8	99.7	>99.9	>99.9	95.3	>99.9	>99.9	>99.9	98.1	0.2	99.6
98	406	99.5	98.0	99.8	99.9	91.5	>99.9	>99.9	>99.9	96.5	0.3	99.2
99	406	97.2	97.6	98.6	98.9	81.6	>99.9	>99.9	>99.9	92.4	N.D.	97.6
100	407	99.4	99.3	99.9	99.9	91.5	>99.9	>99.9	>99.9	96.6	0.2	99.2
101	407	98.8	98.8	99.6	99.7	88.0	>99.9	>99.9	>99.9	95.1	N.D.	98.8
102	408	98.5	98.0	99.3	99.5	87.6	>99.9	>99.9	>99.9	95.0	N.D.	98.6
103	409	99.3	99.3	99.7	99.8	91.6	>99.9	>99.9	>99.9	96.7	N.D.	99.2
104	409	99.2	99.1	99.7	99.8	90.3	>99.9	>99.9	>99.9	96.5	N.D.	99.1
105	409	98.8	98.4	99.3	99.6	88.6	>99.9	99.9	>99.9	95.1	0.1	98.7
106	410	99.1	99.2	99.6	99.8	89.6	>99.9	>99.9	>99.9	95.8	0.4	99.0
107	410	98.0	98.1	98.9	99.1	86.2	99.9	>99.9	96.0	94.6	0.2	98.1
108	411	99.4	99.4	99.7	99.8	91.6	>99.9	>99.9	>99.9	96.7	0.3	99.2
109	411	99.3	99.3	99.7	99.8	91.3	>99.9	>99.9	>99.9	96.5	0.2	99.1
110	411	97.7	97.9	98.7	98.9	84.0	99.7	99.9	99.6	93.8	0.3	97.8
111	411	97.5	97.8	98.6	98.8	81.0	99.7	99.9	99.6	92.4	0.2	97.6
112	411	99.2	99.0	99.7	99.8	90.6	>99.9	>99.9	>99.9	96.4	0.3	99.1
113	411	99.8	99.6	99.9	99.9	94.6	>99.9	>99.9	>99.9	97.4	0.3	99.5
115	411	99.6	99.6	99.9	99.9	93.4	99.9	>99.9	>99.9	97.0	0.2	99.4
116	411	98.8	98.8	99.4	99.5	89.4	>99.9	>99.9	>99.9	96.1	0.4	98.8
117	411	97.8	98.0	98.8	99.0	83.7	99.9	>99.9	99.7	93.7	N.D.	97.9
118	411	99.2	99.1	99.6	99.7	90.1	>99.9	>99.9	>99.9	96.0	N.D.	99.0
119	411	98.9	99.1	>99.9	99.6	90.1	99.9	>99.9	>99.9	95.9	0.1	98.9
130	411	99.2	99.2	99.7	99.8	89.6	>99.9	>99.9	>99.9	96.5	0.4	99.0
131	411	99.7	>99.9	99.9	99.9	95.1	>99.9	>99.9	99.1	97.6	0.3	99.5
132	411	98.8	>99.9	99.4	99.6	89.2	>99.9	>99.9	>99.9	96.3	0.4	98.8
133	411	99.2	>99.9	99.8	99.7	94.7	>99.9	>99.9	>99.9	98.0	0.7	99.3
134	411	97.9	>99.9	98.6	99.0	87.4	>99.9	>99.9	>99.9	96.0	0.5	98.3
135	411	98.7	>99.9	99.4	99.5	90.5	>99.9	>99.9	99.0	97.5	0.6	98.8
137	411	>99.9	98.1	>99.9	>99.9	>99.9	99.9	99.9	>99.9	>99.9	N.D.	99.9
138	411	99.5	>99.9	99.8	99.7	95.6	>99.9	>99.9	>99.9	97.6	N.D.	99.5
139	411	99.9	>99.9	>99.9	99.9	99.2	>99.9	99.9	99.9	99.6	0.3	99.9
140	411	99.6	98.9	99.8	99.9	95.3	99.8	99.8	99.8	97.6	0.5	99.4
141	411	99.6	99.2	99.8	99.9	95.4	>99.9	99.9	>99.9	98.0	0.4	99.5

Time days	Temp	Pentan	2,3 Dimethyl butane	Methyl Cyclo Pentane	Cyclo hexane	Benzene	Ethyl Benzene	m,p Xylene	Cumene	TCE	1,1,2-trichloro ethane	Total
145	415	99.6	96.1	99.8	99.9	97.2	99.9	99.9	>99.9	99.2	0.8	99.6
146	415	98.6	98.5	99.5	99.5	91.6	>99.9	>99.9	>99.9	98.3	0.6	98.9
148	415	99.2	98.7	99.6	99.7	94.5	>99.9	>99.9	>99.9	98.2	N.D.	99.3
150	416	99.3	98.9	99.7	99.7	92.9	>99.9	>99.9	>99.9	97.4	0.6	99.2
152	416	99.2	99.0	99.7	99.7	91.6	>99.9	>99.9	>99.9	97.2	N.D.	99.1
153	416	99.6	99.4	>99.9	99.9	94.4	>99.9	>99.9	>99.9	97.8	0.5	99.5
154	416	97.5	95.7	98.6	99.0	90.3	>99.9	>99.9	>99.9	97.4	0.7	98.4
157	416	99.2	97.8	99.7	99.8	93.3	>99.9	>99.9	>99.9	97.6	0.7	99.2
158	416	99.7	>99.9	>99.9	>99.9	98.5	>99.9	99.8	99.6	99.7	0.3	99.8
159	416	99.4	>99.9	>99.9	>99.9	94.3	>99.9	>99.9	>99.9	97.4	N.D.	99.5
160	416	99.3	96.5	>99.9	>99.9	92.9	>99.9	>99.9	>99.9	97.7	N.D.	99.4
161	416	99.6	99.5	>99.9	>99.9	91.5	>99.9	>99.9	>99.9	96.7	0.1	99.3
162	416	99.6	99.7	>99.9	>99.9	93.2	>99.9	>99.9	>99.9	98.8	N.D.	99.5
163	416	99.1	99.4	99.8	99.9	83.9	>99.9	>99.9	99.0	95.9	0.3	99.0
164	417	98.1	96.8	99.6	99.8	83.0	>99.9	>99.9	>99.9	94.1	N.D.	98.3
165	417	99.5	>99.9	>99.9	>99.9	94.3	>99.5	>99.9	>99.9	97.6	N.D.	99.5
166	417	99.5	>99.9	>99.9	>99.9	75.0	>99.9	>99.9	>99.9	97.8	N.D.	99.6
163	417	99.2	99.5	99.9	99.9	90.3	>99.9	>99.9	>99.9	96.3	N.D.	99.1
169	418	99.6	98.7	>99.9	>99.9	93.5	>99.9	>99.9	>99.9	97.4	N.D.	99.4
170	418	99.6	98.7	>99.9	>99.9	93.5	>99.9	>99.9	>99.9	97.4	N.D.	99.4
171	418	99.7	98.0	>99.9	>99.9	76.3	>99.9	>99.9	>99.9	98.2	N.D.	99.6
172	418	99.3	99.5	99.9	99.9	90.2	>99.9	>99.9	>99.9	96.1	N.D.	99.1
173	418	>99.9	>99.9	>99.9	>99.9	99.4	>99.9	>99.9	>99.9	99.6	N.D.	>99.9
177	418	99.4	99.4	99.8	99.9	91.4	>99.9	>99.9	>99.9	96.5	N.D.	99.2
179	418	99.5	99.6	99.9	>99.9	92.6	>99.9	>99.9	98.2	97.4	N.D.	99.3
181	418	99.6	>99.9	>99.9	>99.9	90.9	>99.9	>99.9	>99.9	96.4	0.3	99.3
182	418	99.4	99.5	99.9	99.9	89.5	>99.9	>99.9	>99.9	96.2	N.D.	99.1
183	418	>99.9	>97.9	>99.9	>99.9	93.8	>99.9	>99.9	>99.9	99.3	N.D.	99.9
184	418	99.9	>99.9	>99.9	>99.9	96.2	>99.9	>99.9	99.2	97.6	N.D.	99.5
185	418	99.9	>99.9	>99.9	>99.9	94.9	>99.9	>99.9	>99.9	98.0	N.D.	99.6
186	418	99.2	99.3	99.8	99.9	89.0	>99.9	>99.9	>99.9	95.9	N.D.	99.0
192	418	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	>99.9	>99.9	0.1	>99.9
193	418	99.9	>99.9	>99.9	>99.9	95.2	>99.9	>99.9	98.8	98.0	N.D.	99.6
194	418	99.0	>99.9	>99.9	>99.9	94.6	>99.9	>99.9	>99.9	97.7	N.D.	99.6
195	418	99.9	>99.9	>99.9	>99.9	94.3	>99.9	>99.9	99.5	97.8	N.D.	99.6
196	418	>99.9	>99.9	>99.9	>99.9	97.7	>99.9	>99.9	>99.9	98.8	N.D.	99.8
197	418	>99.9	>99.5	>99.9	99.9	99.2	>99.9	>99.9	98.3	99.5	N.D.	99.9
198	418	>99.9	>99.9	>99.9	>99.9	99.9	>99.9	>99.9	99.0	99.9	N.D.	>99.9
199	418	99.5	99.6	99.9	>99.9	89.7	>99.9	>99.9	99.1	95.9	N.D.	99.1
200	418	99.8	>99.9	>99.9	>99.9	93.7	>99.9	>99.9	>99.9	97.4	N.D.	99.5
201	418	>99.9	>99.9	>99.9	>99.9	99.7	>99.9	>99.9	>99.9	99.8	N.D.	>99.9
202	418	>99.9	>99.9	>99.9	>99.9	97.0	>99.9	>99.9	>99.9	98.6	N.D.	
203	418	>99.9	>99.9	>99.9	>99.9	98.9	>99.9	>99.9	>99.9	99.4	N.D.	
204	418	99.9	>99.9	>99.9	>99.9	96.1	>99.9	>99.9	99.3	98.4	N.D.	
205	418	99.9	>99.9	>99.9	>99.9	93.7	>99.9	>99.9	>99.9	97.6	N.D.	
206	418	>99.9	>99.9	>99.9	>99.9	99.0	>99.9	>99.9	>99.9	99.4	N.D.	
208	418	99.8	>99.9	>99.9	>99.9	93.6	>99.9	>99.9	>99.9	97.4	N.D.	
209	418	99.8	>99.9	>99.9	>99.9	93.4	>99.9	>99.9	>99.9	97.4	N.D.	
210	418	>99.9	>99.9	>99.9	>99.9	96.4	>99.9	>99.9	>99.9	98.4	N.D.	

Table A-7. Chlorinated Hydrocarbon Conversion Over ARI Catalyst

Time days	Temp C	1,1-dichloro-ethylene	Methylene chloride	1,2-dichloro-ethane	trichloro ethylene	1,1,2-trichloro ethane	Partial Oxidation Products, ppm C2HxCly	Total Conv.
2	350	>99.9	99.3	>99.9	>99.9	0.1	1.6	99.6
3	350	>99.9	99.4	>99.9	>99.9	0.0	1.7	99.6
4	350	>99.9	99.1	>99.9	>99.9	0.0	1.7	99.6
5	350	>99.9	99.2	>99.9	>99.9	0.0	0.0	>99.9
8	350	>99.9	99.1	>99.9	>99.9	0.0	1.4	99.6
9	350	>99.9	99.3	99.9	99.9	0.0	1.5	99.6
10	350	>99.9	99.3	>99.9	>99.9	0.0	1.5	99.6
11	350	>99.9	99.1	>99.9	>99.9	0.0	1.5	99.6
12	350	>99.9	99.2	>99.9	>99.9	0.0	1.2	99.7
13	350	>99.9	99.2	>99.9	>99.9	0.0	1.3	99.7
14	350	>99.9	99.3	>99.9	>99.9	0.0	1.4	99.7
15	350	>99.9	99.2	99.8	>99.9	0.0	1.6	99.6
16	350	99.6	99.3	>99.9	>99.9	0.0	0.0	99.8
17	350	99.7	99.3	>99.9	>99.9	0.0	0.0	99.9
18	350	99.8	99.5	>99.9	>99.9	0.0	0.0	99.9
19	350	99.8	97.7	99.9	>99.9	0.0	0.1	99.7
20	350	99.7	99.6	>99.9	>99.9	0.0	0.0	99.9
21	350	99.8	99.5	>99.9	>99.9	0.0	0.0	99.9
22	350	99.8	99.5	>99.9	>99.9	0.0	0.0	99.9
23	350	99.8	99.5	>99.9	>99.9	0.0	0.0	99.9
24	350	>99.9	99.7	>99.9	>99.9	0.0	0.0	>99.9
25	350	99.8	99.8	>99.9	>99.9	0.0	0.0	99.9
26	350	99.8	99.7	>99.9	>99.9	0.0	0.0	99.9
27	350	99.8	99.7	>99.9	>99.9	0.0	0.0	99.9
28	350	99.7	99.7	>99.9	>99.9	0.0	0.0	99.9
29	350	99.9	96.7	99.8	99.9	0.2	0.0	99.7
30	350	>99.9	97.8	99.9	>99.9	0.1	0.0	99.8
31	350	>99.9	97.9	99.9	99.9	0.2	0.0	99.8
32	350	>99.9	97.4	99.8	99.9	0.2	0.0	99.7
33	350	>99.9	97.9	99.9	>99.9	0.2	0.0	99.8
34	350	99.9	97.9	99.8	99.9	0.2	0.0	99.7
36	350	99.9	97.4	99.6	99.6	0.1	0.0	99.6
37	350	99.9	96.9	99.5	99.7	0.2	0.0	99.6
38	350	>99.9	96.8	99.7	99.8	0.0	0.0	99.7
39	350	99.8	96.3	99.8	99.8	0.0	0.0	99.6
40	350	>99.9	97.0	99.8	>99.9	0.0	0.0	99.8
41	350	>99.9	97.4	99.9	99.9	0.1	0.0	99.8
42	350	>99.9	96.9	99.9	99.9	0.1	0.0	99.8
43	350	>99.9	98.8	>99.9	99.9	0.0	0.0	99.9
44	350	>99.9	>99.9	>99.9	>99.9	0.4	0.0	99.9
45	350	>99.9	97.7	99.9	>99.9	0.0	0.0	99.9
49	350	99.8	97.4	99.8	99.9	0.2	0.0	99.7
50	350	>99.9	97.6	99.7	99.9	0.2	0.0	99.7
55	350	>99.9	97.6	99.9	99.9	0.1	0.0	99.9
56	350	>99.9	97.2	99.9	99.9	0.0	0.0	99.8
57	350	99.8	96.9	99.7	99.7	0.2	0.0	99.6
58	350	99.9	96.6	99.8	99.8	0.3	0.0	99.6
61	350	>99.9	>99.9	99.8	99.9	0.0	0.0	99.9
62	350	99.9	96.4	99.7	99.9	0.1	0.0	99.6
63	350	>99.9	95.6	99.7	99.8	0.4	0.0	99.6
64	350	>99.9	97.2	99.6	99.7	0.2	0.0	99.7
65	350	>99.9	97.3	99.8	99.9	0.2	0.0	99.7
66	350	>99.9	96.8	99.8	99.9	0.1	0.0	99.7
67	350	>99.9	95.6	99.7	99.8	0.0	0.0	99.6
69	350	99.8	95.8	99.3	99.3	0.4	0.0	99.3
70	350	99.9	93.1	99.7	99.8	0.0	0.0	99.7
75	350	>99.9	96.0	99.5	99.8	0.1	0.0	99.6
76	350	>99.9	95.6	99.6	99.8	0.3	0.0	99.6
77	350	>99.9	95.4	99.6	99.8	0.4	0.0	99.5
78	350	>99.9	94.9	99.6	99.7	0.2	0.0	99.5
79	350	>99.9	94.4	99.6	99.7	0.0	0.0	99.5
80	350	>99.9	95.2	99.7	99.8	0.4	0.0	99.5
81	350	>99.9	96.7	99.8	99.8	0.1	0.0	99.7
82	350	>99.9	94.2	99.6	99.7	0.2	0.0	99.5

Table A-7 (continued)

Time days	Temp C	1,1-dichloro-ethylene	Methylene chloride	1,2-dichloro-ethane	trichloro ethylene	Partial Oxidation Products, ppm 1,1,2-trichloro ethane	C2HxCly	Total Conv.
83	350	>99.9	94.8	99.7	99.7	0.2	0.0	99.5
84	350	>99.9	94.6	99.6	99.7	0.2	0.0	99.5
85	350	>99.9	95.2	99.7	99.8	0.1	0.0	99.6
86	350	>99.9	98.4	99.9	>99.9	0.0	0.0	99.9
87	350	>99.9	99.3	>99.9	>99.9	0.0	0.0	>99.9
88	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
89	350	>99.9	>99.9	99.9	>99.9	0.0	0.0	>99.9
90	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
91	350	>99.9	>99.9	99.9	>99.9	0.0	0.0	>99.9
92	350	>99.9	>99.9	99.9	>99.9	0.0	0.0	>99.9
93	350	>99.9	99.6	>99.9	>99.9	0.0	0.0	>99.9
94	350	>99.9	99.6	>99.9	>99.9	0.0	0.0	>99.9
95	350	>99.9	99.1	>99.9	99.9	0.0	0.0	99.9
96	350	>99.9	99.6	>99.9	>99.9	0.0	0.0	>99.9
97	350	>99.9	99.6	>99.9	>99.9	0.0	0.0	>99.9
98	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
99	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
100	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
101	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
102	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
103	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
104	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
105	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
106	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
107	350	>99.9	95.8	99.8	99.8	0.0	0.0	99.7
108	350	>99.9	94.8	99.7	99.7	0.0	0.0	99.6
109	350	>99.9	94.6	99.6	99.7	0.2	0.0	99.5
114	350	>99.9	95.6	99.6	99.6	0.1	0.0	99.6
115	350	>99.9	94.0	99.6	99.7	0.3	0.0	99.4
116	350	>99.9	93.0	99.6	99.3	0.0	0.0	99.3
119	350	>99.9	>99.9	99.7	99.7	0.2	0.0	99.8
120	350	>99.9	95.6	99.8	99.7	0.0	0.0	99.6
121	350	>99.9	95.1	99.7	99.6	0.3	0.0	99.5
122	350	>99.9	93.3	99.5	99.2	0.0	0.0	99.3
123	350	>99.9	93.8	99.6	99.4	0.3	0.0	99.4
124	350	>99.9	95.4	99.7	99.7	0.2	0.0	99.6
125	350	>99.9	95.4	99.8	99.7	0.1	0.0	99.6
127	350	>99.9	94.5	99.4	99.4	0.6	0.0	99.3
128	350	>99.9	>99.9	99.5	99.2	0.2	0.0	99.7
129	350	>99.9	>99.9	99.7	99.4	0.3	0.0	99.7
130	350	>99.9	>99.9	99.6	99.2	0.2	0.0	99.7
131	350	>99.9	93.7	99.6	99.2	0.2	0.0	99.3
132	350	>99.9	94.7	99.7	99.6	0.2	0.0	99.5
133	350	>99.9	>99.9	>99.9	>99.9	0.0	0.0	>99.9
134	350	>99.9	>99.9	>99.9	99.3	0.0	0.0	99.8
135	350	>99.9	93.9	99.7	99.3	0.0	0.0	99.4
136	350	>99.9	96.1	99.9	99.4	0.5	0.0	99.5
137	350	>99.9	95.8	99.8	99.4	0.5	0.0	99.5
138	350	>99.9	95.6	99.8	99.4	0.4	0.0	99.5
139	350	>99.9	94.0	99.5	99.2	0.0	0.0	99.4
141	350	>99.9	93.2	99.6	99.2	0.1	0.0	99.3
142	350	>99.9	92.9	99.6	99.2	0.0	0.0	99.3
144	350	>99.9	92.7	99.5	99.1	0.0	0.0	99.3
145	350	>99.9	94.3	99.7	99.3	0.0	0.0	99.5
146	350	>99.9	94.2	99.7	99.2	0.0	0.0	99.4
147	350	>99.9	92.2	99.4	98.7	0.0	0.0	99.1
148	351	>99.9	93.7	99.6	99.2	0.0	0.0	99.4
150	351	>99.9	93.7	99.6	99.1	0.0	0.0	99.4
151	351	>99.9	93.0	99.6	99.0	0.0	0.0	99.3
152	351	>99.9	93.3	99.6	99.0	0.0	0.0	99.3
153	351	>99.9	93.7	99.6	99.0	0.0	0.0	99.3

86

APPENDIX B

RTI PROTOCOL FOR CATALYST EVALUATION

APPENDIX B

RTI PROTOCOL FOR CATALYST EVALUATION

Several factors need to be considered in evaluating a catalyst for VOC oxidation. These are summarized below.

A. CATALYST SELECTION

The catalysts used for VOC oxidation can be divided into two broad categories: (1) metal oxides and (2) supported noble metal catalysts. The choice of a catalyst should depend on the type and concentration of VOCs to be oxidized. This is because the activity, selectivity, and stability of a catalyst is very sensitive to the feed composition. For example, some of the catalysts may deactivate rapidly if exposed to halogenated or sulfur-containing compounds. Thus, if the feed gas stream will contain any of these compounds, catalysts that are resistant to these compounds and products formed from these compounds should be used.

B. REACTOR DESIGN

Each catalyst is designed to be used for a specific space velocity which is recommended by the vendor.[1] Once the total gas flow to be oxidized is known, the amount of catalyst required can be calculated. The total gas flow will also determine the system design such as the reactor and the tubing size. Most of the catalysts are available in the form of 1/8- or 1/4-inch pellets. The particle size should be selected based on the pressure drop in the reactor and the mass transport limitations. For example, the pressure drop is inversely proportional to the particle size; however, the transport limitations are directly proportional to the particle size. If the transport limitations are significant, the entire catalyst will not be utilized for the reaction resulting in wastage of the catalyst. Thus, the catalyst particles should be as small as possible, provided the pressure drop is acceptable. The reactor design should be such that the ratio of the reactor diameter to particle diameter is greater than 10 to avoid channeling of the gas. Also, the catalyst bed height to bed diameter should be greater than one to avoid end

---

[1]space velocity = gas flow rate/catalyst volume

effects. A gas distributor should be placed on the upstream side of the catalyst to provide a good gas distribution to the catalyst.

C. CATALYST PRETREATMENT

Many catalysts require special treatment before they can be used. The pretreatment procedures may be different for different catalysts. For example, some catalysts may have to be calcined in situ. All the catalysts tested in this work did not require any special activation procedure. However, a general pretreatment procedure was used for evaluating all catalysts in this work.

In general, the catalysts should be heated in dry air, free of organics, to the reaction temperature. When the reaction temperature is reached, the gas can be switched to humidified air which is loaded with the VOCs. The reason for heating the catalyst in dry air from startup is that the cold catalyst can absorb moisture and organics. The adsorption of moisture at low temperature may cause a loss in the catalytic activity because of the formation of new phases. Similarly, the catalyst can adsorb organic matter at low temperature. When the reaction temperature is reached, these VOCs will be combusted resulting in a high temperature increase which can damage the catalyst.

D. ACTIVITY MEASUREMENT

When the VOCs containing air are passed over the catalyst at the reaction temperature, the VOCs will be converted to total oxidation products such as CO_2 and H_2O. However, the catalyst may take some time to achieve stable activity and selectivity. For example, the UCI G-43A catalyst shows an increase in activity for 1 to 2 days before a steady activity is reached. Once the stabilization is achieved, action can be taken depending on the results. For example, if the conversion is less than desired, the temperature can be increased in steps until the desired conversion is achieved. The temperature increase required to achieve the desired conversion will depend on the type of VOC and the type of catalyst. Once the temperature is increased, some time should be allowed for stabilization before any further action is taken.

The validity of the data collected from a continuous reactor is jeopardized if a power failure causes the run to stop. For example, the reactor temperature will drop in the event of a power failure. However, the flow of humidified air containing organics will

continue to flow over the catalyst resulting in a probable damage to the catalyst. Thus, the system should be designed such that it allows an inert gas to flow over the catalyst during a power failure.

E. CATALYST DEACTIVATION

During operation, both the catalyst activity and selectivity may decrease with time. For example, the total conversion of the hydrocarbons may decrease below the desired level. Also, some undesirable partial oxidation products may form as the catalyst ages. These products may be more toxic than the original organics in the air. The catalyst temperature can be increased periodically to compensate for the loss in catalytic activity. The temperature increase required to maintain a constant conversion will depend on the mechanism of deactivation.

Since the oxidation is an exothermic reaction, considerable heat is liberated in this reaction. This will result in an increase in the catalyst temperature. The heat liberated depends on the concentration of the VOCs in the air. The gas temperature is increased by about 0.23 °F per ppm of hydrocarbon, if the compound is completely combusted to CO_2 and H_2O, assuming the heat of combustion at 18,000 Btu/lb of HC. Thus, with 500 ppm of C_6 hydrocarbons in the air, the gas temperature will increase approximately 115 °F. This rise will be smaller for C_1-C_2 chlorinated compounds. Care should be taken that the catalyst temperature does not exceed the maximum recommended temperature.

F. MASS BALANCE

A carbon balance should be established for the overall reaction. The carbon balance is based on the total carbon atoms in the feed gas and the total carbon atoms accounted for in the effluent. A carbon balance within $\pm$ 5 percent can be considered as reasonably good within experimental errors. If the balance cannot be accounted for within $\pm$ 5 percent, then attempts must be made to account for the difference. For example, some partial oxidation products containing carbon may be formed that may be more toxic than the original compounds. Also, some carbon may be deposited on the catalyst surface that will ultimately result in catalyst deactivation.

If the organics contain hetero-atoms such as halogens or sulfur, a balance on these atoms should also be established. However, sometimes this may be difficult because of analytical problems. For example, chlorine balance is very difficult because of the analytical problems in accurately determining Cl_2 and HCl. Retention of hetero-atom containing compounds on the catalyst surface is one of the modes of catalyst deactivation. While deactivation by coking is generally reversible, the deactivation by hetero-atom poisoning can be reversible or irreversible. Thus, a mass balance can be useful in understanding and possibly overcoming the deactivation. For example, a catalyst deactivated due to coking can be regenerated by burning the coke at high temperature.

G. POST-RUN ANALYSIS

Once the catalyst temperature reaches the maximum vendor-recommended temperature, the operation should be stopped. Although some catalysts can be used above the maximum recommended temperature, it is not recommended because the deactivation may be very rapid above this temperature. The catalyst should be cooled to room temperature in an organic-free dry air. The used catalyst can be investigated by chemical and physical analysis to understand the mechanism of deactivation.

H. ECONOMIC EVALUATION

Various factors should be considered to compare the economics of operation of different catalysts. These are the auxiliary fuel costs that are determined by the reactor temperature, electricity costs for air flow, and the catalyst replacement cost. Auxiliary fuel cost is the largest single operating cost for all systems. Catalyst deactivation causes more fuel to be used to maintain constant conversion with time. A more expensive catalyst can be economically competitive if it can be operated at a low temperature for a long time. Thus, the primary electrical costs are for the fan used for air flow through the unit. Because the pressure drop is generally higher for a fluid bed than a fixed bed, the electrical costs are somewhat higher for a fluid bed than for the fixed-bed operation.

APPENDIX C

STANDARD TEST METHOD FOR EVALUATING OXIDATION CATALYSTS

APPENDIX C

STANDARD TEST METHOD FOR EVALUATING OXIDATION CATALYSTS

The following method was used to evaluate the catalysts for VOC oxidation in RTI's study.

1. Each catalyst was crushed in a porcelain mortar and pestle.

2. The crushed catalyst was sieved to small particles to ensure a tube diameter to particle diameter ratio of at least 10.

3. A portion of this material was subjected as needed to chemical analysis including:

   - XRD,
   - ESCA,
   - BET, and
   - Mercury Porosimetry.

   NOTE: The operating conditions of the microreactor were chosen to simulate commercial conditions. The vendor's recommendations on these conditions follow:

	Space velocity (h^{-1})	Temperature (°C)	
		Initial	Maximum
G-43	5,000-10,000	427-538	NA^a
Carulite	15,000	315	500
CK-302	3,600	350	600
ARI	12,000	350	NA

^{a}Not available.

4. The sieved catalyst was loaded into the quartz tube reactor (4 mm ID) supported by quartz wool plugs. To ensure close packing the reactor was tapped lightly as the material was loaded. The amount of catalyst added was dictated by the space velocity recommended by the catalyst vendors. This varied from catalyst to catalyst.

93

5. The reactor was then heated to the recommended initial temperature under conditions given by each individual vendor. Typically this was done while passing air through the reactor.

6. When the recommended reactor temperature was reached, the flow of VOC-containing gas mixture containing water vapor and the VOCs was begun.

7. Chemical analysis (gas chromatography) was used to determine if the desired level of conversion of the VOC is attained at the initial temperature. If not, the temperature was raised until the conversion did equal the design level.

8. Each reactor was sampled periodically to determine its conversion. If conversion dropped, the reactor temperature was raised until conversion again increased to the desired level.

9. The reactor temperature was recorded as a function of time by a data logger from where the data were stored both on a hard disk (PC) and on hard copy.

10. At the end of the run, the catalyst was cooled in a nitrogen flow.

11. The 'spent' (deactivated) catalyst was subjected to the same battery of tests listed in step (3).

APPENDIX D

LITERATURE REVIEW "DEACTIVATION OF OXIDATION CATALYSTS"

APPENDIX D
LITERATURE REVIEW: "Deactivation of Oxidation Catalysts"

Prepared by
James J. Spivey
Research Triangle Institute
John B. Butt
Northwestern University

This literature review is focused on the deactivation processes occurring on oxidation catalysts used to control volatile organic compounds (VOCs). General reviews of the use of catalytic oxidation for VOC control are available (Spivey, 1987) as are basic assessments of the use of catalytic oxidation for control of industrial emissions (Palazzolo et al., 1984).

The latter work contains a review of catalytic incineration technology to 1984 and a series of evaluations of test data at operating sites including can coating, coil coating, and printing plants. Although that work uses the term "incineration" rather than "catalysis", its content is catalytic and it presents an interesting overview of some applications to that date. Texts on the general subject of catalyst deactivation are available (Butt and Petersen, 1988; Hughes, 1984; Hegedus and McCabe, 1984) and provide an excellent framework in which to study the various deactivation processes occurring on the working catalyst. However, we are aware of no systematic review of the deactivation processes occurring on oxidation catalysts at conditions typical of field practice with VOCs.

Many studies have been made on the deactivation of automotive catalysts (e.g., Shelef et al., 1978), but these generally operate at higher temperatures and with different inlet gas compositions than considered herein. There is substantial literature dealing with catalysis of NO oxidation on these catalysts, most of which is not included in the scope of this report. One interesting composition, reported to be resistant to arsenic and sulfur poisoning, is composed of mordenite with $SiO_2/Al_2O_3 > 10$ loaded with transition metals such as Cu, W, V or Fe mixed with MoO_3 (Tejima et al., 1988). Application of such catalysts to VOC oxidation would depend upon the stability of the zeolite under reaction conditions, however the deactivation resistance is of general interest.

This review is organized by catalyst type. For VOC oxidation, these catalysts can be roughly divided into three main classes: supported noble metals, single/mixed metal oxides and noble metal/metal oxide combinations. In general, supported noble metals consist of highly dispersed small crystallites on metal oxide supports as -alumina. Typical metal loadings are less than 1% by weight. Single/mixed metal oxide catalysts may be either supported on an oxide like -alumina or used as bulk unsupported oxides. The metal loading of supported oxide catalysts is typically much greater than for noble metals, due to their generally lower inherent activity per exposed atom of catalyst. However, for some applications, this higher overall loading for metal oxide

catalysts makes them more tolerant of catalyst poisons since some compounds, even at low concentrations, may quickly poison the limited number of noble metal oxidation sites present in supported noble metal catalysts. Oxidation catalysts have also been developed that contain both a noble metal and a metal oxide. An example is the 0.1% Pt/3%NiO (on -alumina) catalyst developed by UCI (Louisville, KY). However, little is reported on the systematic studies of the deactivation processes occurring on these catalysts at conditions of interest. Thus, only supported noble metal and metal oxide catalysts are considered here.

Catalysts of both types have found application in the field for control of VOCs. Examples include the chromia/alumina catalyst of ARI International (Palatine, IL), the mixed metal oxide catalyst of Dedert Topsoe (Des Plaines, IL), noble metal catalysts of UCI (Louisville, KY) and promoted hopcalite of Carus Chemical (LaSalle, IL). [These catalysts are generally not marketed directly to users, but are part of a hardware package designed by others.]

No attempt is made in this review to examine the many types of mathematical models that have been applied to deactivation (this subject is well covered in the work of Butt, e.g., Butt, 1972 and Butt and Petersen, 1988) nor the molecular details of the several mechanisms (e.g., sintering) that collectively constitute the observable deactivation processes for VOC's in general. Instead, the review focuses on the results reported on various catalysts of commercial interest and work that has been done on control of VOCs of interest to the Air Force, especially chlorinated hydrocarbons.

Conclusions from this review include the following:

(1) Chlorinated compounds are generally poisons for supported noble metal catalysts. However, the interaction of the chlorine with the noble metal (and sometimes the support) is complex and, in some cases, reversible. The HCl or Cl_2 produced by the oxidation reaction itself may be the catalyst poison in some cases. On metal oxides, chlorine atoms may form volatile compounds that lead to loss of the metal (e.g., for chromia on alumina).

(2) Reversible inhibition of oxidation activity by water vapor, either produced in the reaction or present in the inlet gas, is often observed. This inhibition is particularly pronounced for metal oxide catalysts.

(3) Sulfur deactivates both noble metal and metal oxides but by apparently different mechanisms. On noble metals, the sulfur retained on the catalyst may be desorbed at elevated temperatures, sometimes with little loss of activity. On metal oxides, however, the sulfur may be incorporated within the catalyst as a sulfate, which may be irreversible.

(4) Deactivation of oxidation catalysts tends to change both activity and selectivity over time. Decreases in activity (i.e., overall conversion) are usually straightforward. However, these decreases may be accompanied by changes in reaction product

97

distribution (i.e., exit gas composition). Specific examples include the production of formaldehyde in the oxidation of methane (Cullis et al., 1970) and Cl_2 (rather than HCl) from the oxidation of chlorinated compounds (Ramanathan and Spivey, 1989).

NOBLE METAL CATALYSTS

Supported Platinum Catalysts

One of the most widely used catalysts for control of many types of gaseous emissions is platinum supported on various oxides such as -alumina. Platinum is one component of automotive exhaust catalysts (Shelef et al., 1978) and is widely applied to gases containing strictly hydrocarbon (and oxygenated hydrocarbon) compounds. Because platinum, as a general rule, is poisoned by chlorinated hydrocarbons, research on the use of these catalysts to oxidize chlorinated contaminants in air is limited. However, some important results are available.

Bond and Sadeghi (1975) studied the oxidation of a number of chlorinated hydrocarbons over a series of Pt/-alumina catalysts at 420-500°C. At an inlet concentration of more than 13,000 ppm perchloroethylene (C_2Cl_4), no deactivation was observed over a 0.8% Pt/-alumina catalyst during a period of 12 hours at a conversion of 95%. This lack of deactivation, which would almost certainly be observed at longer reaction times, may be due to the unusually high platinum loading.

Deactivation of Pt/alumina catalysts has been observed by Lindberg et al. (1977) in the oxidation of chlorinated hydrocarbons. In this case a commercial Houdry "3K" catalyst containing 0.2% chlorine and 0.6% Pt (on alumina) was used in the oxidation of a gas containing around 18,000 ppm C_1 - C_2 chlorinated hydrocarbons (in 87% nitrogen/11% oxygen). both saturated and unsaturated C_2 compounds were used. The deactivation appeared to be particularly noticeable at temperatures less than 300°C and when less than stoichiometric oxygen was available. The authors stress the importance of adequate preheating of the gas before it comes into contact with the leading edge of the catalyst bed in preventing deactivation by carbon deposition. At temperatures between 425 and 458°C, less than 1 ppm vinyl chloride was observed in the exit gas when an inlet gas containing 96% nitrogen, 3.8% oxygen, and 0.2 - 0.6% vinyl chloride was oxidized at 4000 - 6000 hr^{-1} space velocity. At the same space velocities and inlet gas concentration the catalyst deactivated rapidly at temperatures below 400°C. In related work, Yang and Reedy (1977) observed deactivation of a Pt/alumina catalyst at 275°C in the oxidation of vinyl chloride but deactivation was not reported at temperatures between 322 and 343°C. This suggests that deactivation on platinum/alumina catalysts accelerates at lowers temperatures, possibly because of increased retention of HCl produced by the oxidation process. Indeed, Dalton and Sircar (1981) report that deactivation of a 5% Pt/carbon catalyst could be minimized by operating at temperatures above 300°C and explicitly suggest that these higher temperatures limit HCl from interacting strongly with the catalyst surface. Mendyka and Rutkowski (1984) studied the deactivation of Pt oxidation catalysts by HCl. Their conclusions were that low Pt contents (0.15 - 0.30%, presumably on Al_2O_3) were resistant to poisoning, but

98

that the metal content was still sufficient to promote oxidation. They also report a Pt-Pd bimetallic that is said to be resistant to HCl.

Volter et al. (1987) carried out an interesting study examining in more detail the interaction of chloride with $Pt/-Al_2O_3$ catalysts. Catalysts were prepared with and without intentionally added chloride (this was done by changing the way the alumina was impregnated with platinum). They then used these catalysts to study the total oxidation of n-heptane and examined the effect of the chloride on the deactivation and oxidation processes. Calcination of the catalysts, which involves heating them in an oxidizing environment after their preparation, was studied to help understand the relationship between chloride content, temperature history, and total oxidation activity. Chloride-free catalysts, designated [Pt] calcined in air at temperatures between 500 and 1000°C, showed little variation in conversion of n-heptane with increasing calcination temperature, whereas the chloride-containing catalysts, designated $[Pt_{cl}]$, showed increased conversion with increasing calcination temperature, though the $[Pt_{cl}]$ catalysts were not as active as [Pt]. This suggests a poisoning effect of the chloride. Interestingly, however, this effect was not universal. When two chloride-free [Pt] catalysts, previously calcined at 500 and at 1000°C, were impregnated with HCl and recalcined at 550°C, only the [Pt] catalyst first calcined at 500°C was poisoned, the [Pt] catalyst first calcined at 1000°C was as active as before the aqueous HCl treatment. Measurement of metal dispersion was made to see if this difference in poisoning was related to crystallite size. Except at a calcination temperature of 900°C, dispersion tests showed the [Pt] sample to be much less dispersed than the $[Pt_{cl}]$ sample, i.e., the platinum crystallites on the alumina surface of the [Pt] catalyst were larger and fewer in number than on the $[Pt_{cl}]$ catalyst. The dispersion of both catalysts decreased with calcination temperature.

Previous work by some of the same authors (Lieske et al., 1983; Lietz et al., 1983) has shown that the platinum metal in a highly dispersed platinum/alumina catalyst is transformed to an oxidized Pt (IV) surface complex at 500°C. Higher temperatures cause a decomposition of this complex into a poorly dispersed metallic crystalline platinum designated $[Pt_{cl}]$. Both types of platinum catalyze the oxidation of hydrocarbons such as n-hexane, but $[Pt_{cl}]$ is much more active. Volter et al. (1987) thus state that the chloride-containing catalyst $[Pt_{cl}]$ calcined at 500°C contains only the oxidized Pt (IV) surface complex and is thus less active. Increasing calcination temperature of the $[Pt_{cl}]$ causes formation of $[Pt_{cl}]$ crystallites, resulting in higher oxidation activity.

The effect of chlorine on the catalyst dispersion and activity is interesting. Lieske et al. (1983) showed that chloride promotes redispersion of platinum crystallites by transforming $[Pt_{cl}]$ into Pt (IV). Guo et al. (1988) conclude, from an examination of Pt/Al_2O_3 catalysts treated with CCl_4, C_2HCl_3, HCl, and H_2O, that in an oxidizing environment at 550°C, both sintering and redispersion occur and may explain the differing effects of chlorine on these catalysts. The oxygen dissociates some of the Pt crystallites into molecular Pt oxide species which migrate across the surface. Some of these species are incorporated into other Pt crystallites while other Pt oxide species are trapped on support sites where chlorine is present. Butt and Petersen (1988, pp. 226-229) discuss the available literature on this redispersion process and the role of the alumina support in promoting it. Volter et al. (1987) found that a highly dispersed

99

platinum/alumina catalyst is more sensitive to chloride poisoning than a sintered catalyst, as expected if a chloride-promoted [Pt.] → Pt (IV) transformation precedes the redispersion. Thus, chloride may not only poison platinum catalysts but may also aid in redispersion of the platinum at high temperatures. For some reactions, such as oxidation, the highly dispersed form of the catalyst is less active than the catalyst containing larger metallic crystallites.

In addition to chlorinated compounds, other types of compounds that may be present in air strippers also poison noble metal catalysts. Principal among these are sulfur-containing compounds such as H_2S. A number of studies have examined the interaction of sulfur with platinum catalysts. Kawahata and Lazzaro (1981) studied the effect of H_2S on the oxidation of methane using a catalyst described only as a "finely divided platinum or palladium catalytic surface covering an inner platinum wire". This catalyst is used as a sensor for methane in air. Exposure to 342 ppb H_2S reduced the sensor response, which is a measure of the methane oxidation activity, to 80% of the original response in 55 hours. Unfortunately, no attempt was made to examine the cause of the deactivation or to restore its activity. However, the use of activated carbon upstream of the catalyst (to adsorb H_2S) decreased the rate of deactivation, with the catalyst maintaining 91% of the original activity after 280 hours exposure to a challenge gas concentration of 350 ppb H_2S. Sadamori et al. (1981) also studied the oxidation of methane in air. Challenging a Pt-Al_2O_3 catalyst with an inlet air stream containing 1% methane and 5-10 ppm sulfur, they found that the conversion dropped from 95.5% to 80.8% over a period of 5532 hours. The form of the sulfur is not specified; it is presumably H_2S. The authors developed a new alumina fiber catalyst, presumably based on supported platinum (though few details are given) that maintained 97.4% conversion after 4735 hours in a stream with 2 ppm sulfur. It is implied, though not specifically stated, that the reason for this enhanced resistance to deactivation by sulfur is the ability to maintain high catalyst dispersion on a support with high specific surface area and to minimize loss of noble metal by vaporization at high temperatures.

The interaction of poisons such as sulfur with platinum catalysts is also affected by operating temperature, as discussed above for chlorine. In a series of studies at Warren Spring Laboratory in England, the deactivation of platinum catalysts by sulfur compounds was studied (Irwin et al., 1979; Heyes et al., 1982a,b; Pope et al., 1978). Using methyl mercaptan and dimethyl sulfide, the deactivation was studied at various temperatures. Irwin et al. (1979) found that dimethyl sulfide deactivated three forms of supported platinum catalysts: a monolith, a crimped alloy ribbon, and conventional platinum on alumina spheres. Using the monolith catalyst (a Pt-Thermacomb, registered trademark of 3M), oxidation of 8 ppm dimethyl sulfide (in air) at 138°C and 10^4 hr^{-1} space velocity resulted in a gradual increase in outlet concentration of dimethyl sulfide and simultaneous decrease in SO_2 concentration (SO_2 being one product of dimethyl sulfide oxidation). Reactivation of the catalyst at 350°C for 17 hours in air resulted in a catalyst that showed no deactivation at 170°C for 3 hours at the same space velocity. Using nominally the same catalyst, Heyes et al. (1982a) studied the oxidation of a mixture 100 ppm of methyl mercaptan and 100 ppm of n-butanal in air. Over a 100-hour test at 400°C, no deactivation of the platinum-Thermacomb was observed, though little SO_2 appeared in the outlet. Heyes et al. suggest that part of the sulfur was converted to SO_3 and some was "stored in some form in the catalyst". Unfortunately, SO_3 analyses were not reported. Such analyses would

provide a way to distinguish between SO_3 production and retention of sulfur by the catalyst. If the sulfur is retained by the catalyst rather than being continuously converted to SO_3, deactivation must eventually occur. The deactivation observed by Irwin et al. (1979) at a much lower temperature (138°C) may thus have occurred more rapidly because the sulfur is retained by the catalyst more readily at lower temperatures. However, in whatever form the sulfur is retained, it appears to be removed by higher temperatures. Finally, Pope et al. (1978), again using a nominally identical Pt-Thermacomb catalyst, examined dimethyl sulfide oxidation at temperatures from 200 to 450°C, 25,000 hr^{-1} space velocity, and an inlet concentration of 100 ppm. As observed by Heyes et al. (1982a), sulfur present in the inlet gas as dimethyl sulfide could not be fully accounted for by SO_2 in the outlet gas. Also as before, SO_3 was not measured and may account for all or part of the sulfur not accounted for as SO_2. Interestingly, Pope et al. (1978) observed that at 265°C essentially all the sulfur could be accounted for as SO_2, but at either lower or higher temperatures, it could not. Based on other results, they suggest that elemental sulfur is not dep sited on the catalyst at higher temperatures, implying that it is converted to SO_3. Rossin (1989) also found no deactivation in the oxidation of up to 250 ppm diethyl sulfide in dry air over a commercial 1 % Pt/-Al_2O_3 catalyst for up to 100 hours. Temperatures between 225 and 300°C were investigated. Sulfur balances (as SO_2 only, SO_3 was not measured) were typically 85 %, which, together with the lack of any deactivation, suggests that SO_3 was formed. However, the observed zeroth reaction order in diethyl sulfide also suggests strong adsorption of this reactant.

High operating temperatures, even in the absence of poisons, may deactivate platinum catalysts by several mechanisms. These include sintering and slow vaporization of the platinum metal itself. Many studies have focused on this, and only a few are noted here. Wanke and Flynn (1975) provide a review of sintering of supported metals. Butt and Petersen (1988, pp. 172- 232) also discuss sintering, including a valuable critique of ways to measure it. Sadamori et al. (1981) examined the effect of heating in air at 600°C on two platinum/alumina catalysts used for methane oxidation. Methane oxidation activity dropped by roughly an order of magnitude over a period of 1000 hours for both catalysts. Continuous oxidation of natural gas (containing 88% methane, 6% ethane, 4% propane, 2% butane and 2 ppm sulfur) for 4750 hours resulted in no loss of activity for a platinum catalyst on a high surface area support (neither the operating temperature nor the specific properties of the catalyst are not reported).

In an EPA-sponsored field test of an Engelhard catalyst system, a "precious metal" catalyst on an alumina/monolith support was used to oxidize emissions from a plastics printing plant containing ethanol, n-propanol, and n-propyl acetate (Martin, 1981). Over several month's operation, a drop in conversion was observed at each of the three temperatures studied, 260°C, 315°C, and 370°C. Deactivation (i.e., decrease in conversion) was much less at 260°C than at 370°C. Interestingly, the deactivation was also compound specific, with separate studies on the new and deactivated catalyst showing that n-heptane conversion decreased faster with time than n-propyl acetate conversion. No further explanation of the reason for this deactivation is given.

Supported Palladium Catalysts

Though not widely used for catalytic oxidation of VOCs at conditions of interest herein, some research on supported palladium catalysts for this application has been reported. Palladium may also be used with platinum to form a supported bimetallic catalyst that is the basis for automotive exhaust control, where the temperatures and space velocities are normally higher than in typical VOC control systems. As a general rule, platinum is more active for the oxidation of paraffinic hydrocarbons and palladium is more active for oxidation of unsaturated hydrocarbons and CO (Satterfield, 1980) making their use in automotive exhaust control, where all these compounds are present, an obvious choice.

Chlorine deactivation during hydrocarbon oxidation on palladium has probably been studied more extensively than that of other catalyst poisons. [Chlorine can also be intentionally added to palladium catalysts to promote partial oxidation.] Dalton and Sircar (1981) studied the use of a carbon-supported $PdCl_2$ catalyst designed to oxidize "olefinic halides" such as vinyl chloride emissions. The catalyst is rapidly deactivated by vinyl chloride but can be regenerated by exposure to air at near ambient temperatures (below 70°C). Higher temperatures do not restore activity. The addition of water vapor to the inlet gas stream containing vinyl chloride significantly retards the deactivation process without altering the oxidation reaction rate. This beneficial effect of added water vapor is more pronounced at temperatures below 170°C, at which thermal deactivation is still fairly rapid. Unfortunately, the mechanism by which water vapor retards deactivation is not examined.

Cullis et al. (1970) studied the partial oxidation of methane on a PdO sponge catalyst. Methylene chloride, CH_2Cl_2, was added to the inlet gas, which also contained methane. Methane oxidation was strongly inhibited and formaldehyde was formed. The formaldehyde production continued after the CH_2Cl_2 addition was stopped, suggesting a strong interaction of chlorine with the catalyst. However, pulses of pure CH_4 plus O_2 gradually restored the original activity, showing that this effect of interaction is reversible. The authors suggest that the interaction of halocarbons like CH_2Cl_2 with the palladium catalyst would lead to dipoles with the negative charge facing outward. These dipoles would decrease coverage by oxygen and promote the formation of partial oxidation products like formaldehyde. A similar effect would be observed for other gases that create negative dipoles on the surface. This study also serves as a reminder of the possibility of the formation of toxic compounds like formaldehyde that are not present in the inlet gas.

This difference in selectivity was also noted by Hucknall et al. (1980). They looked at methane oxidation on palladium catalysts, in their case using alumina, tin oxide, and titania supports. The effect of chloro-and bromohydrocarbons were examined. The initial effect of methylene chloride and chloroform was to enhance the combustion of methane on 2.7% Pd/-Al_2O_3 at 377°C, though further exposure to these compounds caused deactivation. A striking feature of these results is that there was almost no difference in deactivation among 1,2- dichloroethane, methylene chloride, and methylene bromide for a 2.7% Pd/-Al_2O_3 catalyst, which was the most poison-tolerant catalyst. The degree of deactivation on this particular catalyst was also essentially

independent of temperature in the range 352- 457°C when exposed to chloroform. The activity could be partially regained after flowing helium over the catalyst at 377°C for 16 hours. XPS measurements showed that the effect of the halogens was not only to alter the interaction of palladium and oxygen, but also to promote the formation of a carbon- containing residue. This carbon could be converted to CO_2 in an oxidizing environment. Further study on palladium catalysts by Cullis and Willatt (1983) showed carbon formation from CH_4 when no oxygen was present. Exposure of an unsupported Pd (II) oxide to pure oxygen at 500°C caused rapid loss of CH_4 oxidation activity that could not be restored by reduction in hydrogen. Large clumps of palladium on the catalyst surface, 2 mm in diameter, were observed. However, treatment (in air) of a supported palladium catalyst (2.7% Pd/-Al_2O_3) at 550°C caused an increase in particle size that did not result in a drop in production of carbon oxides from methane. The authors postulate that palladium, unlike platinum, can absorb oxygen into its bulk. This can provide a reservoir of absorbed oxygen to prevent carbonaceous buildup in oxidizing conditions.

Patterson and Kimball (1963) also studied oxidation on palladium catalysts. They examined ethylene oxidation using a palladium film prepared in the presence of HCl. At 155°C, the initial reaction rate of ethylene oxidation on the chlorine- containing catalyst, in their batch experiments, was one-fifth that of one prepared without HCl. There was also a selectivity for acetic acid production with the chlorine-containing catalyst. Complete inhibition of C_2H_4 oxidation on the chlorinated palladium catalyst was found at 240°C when HCl was present in the gas.

In one of few reported studies of a sulfur-tolerant palladium catalyst, Szepesy et al. (1978) report the development of a catalyst consisting of 10^{-6} to 10^{-7} g palladium/g support where the metal is "very highly and uniformly distributed on the support" (no further details of catalyst preparation are given). The catalyst is said to be tolerant of both phosphorous and sulfur-containing compounds. The application of the catalyst to sulfur-containing gases at several plant locations is described, though no detailed activity versus time data is presented. Desai et al. (1987) investigated the use of Pt-Pd catalysts, among others, for the destruction of vapors generated in the disposal of ion exchange resin. A 1% Pt-Pd catalyst was prepared using hollow -Al_2O_3 tubes as supports and the catalyst was exposed to the vapor generated when the resins were oxidized. Unfortunately, the composition of the vapor is not fully known, but presumably it contains both SO_2 and SO_3. The 1% Pt-Pd/-Al_2O_3 catalyst did not deactivate during the two-hour run.

METAL OXIDE CATALYSTS

Metal oxide catalysts for oxidation processes normally consist of oxides of Group IIIB through IIB of the periodic table. As a general rule, these catalysts are more poison- tolerant than supported noble metals, though they are also somewhat less active for oxidation reactions, especially on a per metal atom basis. Metal oxide catalysts can, in principle, be prepared as either bulk oxides of uniform composition or can be supported on less expensive carriers such as -Al_2O_3 which also provide a high specific surface area for the metals.

103

For the purpose of this review, the deactivation of metal oxide catalysts is divided into two sections - single metal oxides and mixed metal oxides. Most catalysts of practical interest are mixed oxides, but research reported on single metal oxides helps provide the framework for understanding the deactivation of mixed oxide catalysts. Butt and Petersen (1988, pp. 128-130) discuss the poisoning of metal oxides.

Single Metal Oxides

Nickel Oxide

Nickel oxide is a well known catalyst for oxidation of methane with steam as well as for the reverse reaction, methanation ($CO + 3H_2 \rightarrow CH_4 + H_2O$). The use of NiO for catalytic oxidation has been less extensively studied though few studies have specifically examined deactivation. Yao and Kummer (1973) looked at the use of NiO crystals as potential components of an automotive exhaust catalyst. In examining the oxidation of C_2 - C_4 hydrocarbons and CO at temperatures between 150 and 400°C, they observed that in the absence of added water vapor in the inlet gas or pre-exposure to water vapor, the oxidation rate initially increased, then decreased rapidly. This activity loss was irreversible at the reaction temperature but could be restored by heating at 500°C or higher in an inert gas or a gas with a few percent oxygen. This deactivation could be avoided altogether by adding 0.1 to 0.5% H_2O in the inlet gas. The authors conclude that the deactivation in the absence of H_2O was caused by H_2O produced by the oxidation of the hydrocarbons or traces of H_2O in the inlet gas. In addition to H_2O, HCl and SO_2 were catalyst poisons. In oxidizing C_2H_4, added SO_2 was taken up by the catalyst (no SO_2 was detected in the outlet gas and the catalyst was poisoned for C_2H_4 oxidation) though the poisoning was not complete even at monolayer coverage. Anhydrous HCl injected into the inlet gas had a similar effect. Both HCl and SO_2 poisoning were completely irreversible by either repeated hydrocarbon oxidation or heating in a few percent oxygen for 48 hours at 800°C. However, washing with concentrated HNO_3 and H_2O could restore activity.

Lavanish and Sare (1977) also report the use of NiO catalysts and the inhibition of oxidation by water vapor. A "hydrated" nickel oxide catalyst, used for vinyl chloride oxidation at 107°C, showed distinct inhibition by water vapor in the inlet gas. The lower the reaction temperature, the greater this inhibition. However, the authors also state that water of hydration is necessary for the catalyst to be active for oxidation. The inhibition by water vapor can be reversed by heating in dry air at 150-200°C. The apparent difference in the effect of water vapor between this study and that of Yao and Kummer (1973) may be due to differences in the nature of the interaction of water vapor and these two catalysts at different temperatures. For example, it might be suggested that the water of hydration, apparently necessary for the NiO catalyst to be active for chlorinated hydrocarbons (as observed by Lavanish and Sare, 1977) was not present at the higher temperatures used by Yao and Kummer, and that this resulted in the deactivation observed in this latter study in the absence of H_2O in the inlet gas. The addition of 0.1 to 0.5% H_2O may have provided this water of hydration even at the higher temperatures, and thus eliminated the inhibition caused by lack of water vapor. The lower temperatures of Lavanish and Sare may cause physisorbed water to condense on the surface, causing distinct inhibition. This

is consistent with the fact that higher temperatures, 150- 200°C, were sufficient to reverse the observed inhibition. Such a temperature is presumably high enough to remove physisorbed water but not the water of hydration. However, alternate explanations, such as a fundamental difference in the crystalline nature of the two NiO catalysts, could also account for the difference in the observed effect of water vapor in these two studies.

The classical case of sulfur poisoning of Ni catalysts is by thiophene, C_4H_4S. This has been reported in detail recently by Megiris and Butt (1988) for Ni/kieselguhr and by Ahmed et al., (1987) for Ni/Al_2O_3. In general, the deactivation is by direct chemisorption on Ni of the sulfur in the thiophene. At temperatures above 150-200°C there is a decomposition of thiophene with a residual Ni-S species (Bourne et al., 1954). The catalyst can be regenerated at higher temperatures in H_2, but at the expense of some sintering of the metal. Oxygen treatment normally leads to the formation of $NiSO_4$ rather than the desorption of SO_2. However, Duprez and Mendez (1987) have shown for Ni/Al_2O_3 that the presence of an unreduced Ni phase improves the thioresistance of the catalyst. Impregnation of Ni on an NiO-Al_2O_3 spinel support led to a formulation that was "particularly resistant" to sulfur poisoning, as measured by thiophene poisoning of the toluene steam reforming reaction at 460°C.

Moon et al., (1987) looked at the carbon-deactivation and regeneration of Ni and Co catalysts. Deactivation (via CO disproportionation) was higher at high temperature (450° versus 300°C) but those catalysts were also more easily regenerated by H_2 treatment. There was some evidence that the nature of the surface was altered by C deposition, perhaps as nickel carbide.

Vanadium Oxide

Vanadium oxide is known to be an active oxidation catalyst for sulfur compounds and is used, with potassium sulfate on a silica support, in the commercial production of sulfuric acid (Satterfield, 1980). It also exhibits some activity for oxidation of hydrocarbons, and V_2O_5 on TiO_2 is used as a commercial catalyst for naphthalene oxidation (Wainwright and Foster, 1979).

Nevertheless, several studies report the deactivation behavior of vanadium catalysts for oxidation of sulfur-containing compounds and hydrocarbons. Heyes et al. (1982a) report the oxidation of both methyl mercaptan and n-butanal on 1% V_2O_5/SiO_2. After an initial induction period, no deactivation was observed for methyl mercaptan oxidation over a 50 hour run, but n-butanal oxidation declined to 75% of the initial level over this same period. Methyl mercaptan oxidation was incomplete even at 430°C (64%) and more CO was produced than CO_2. A shortfall in the sulfur balance also indicated that some sulfur was retained by the catalyst. Desai et al. (1987) report that a 10% V_2O_5/-Al_2O_3 catalyst showed no deactivation when exposed to a gas containing SO_2 and SO_3, among other unspecified contaminants, and was also more active than a 1% Pt-Pd/-Al_2O_3 catalyst. Vassileva et al. (1989) used three catalysts to examine the complete oxidation of benzene. These catalysts were a 30% V_2O_5 on -Al_2O_3, 30% V_2O_5 plus 0.5% Pd on -Al_2O_3, and 0.5% Pd on -Al_2O_3. Using a stoichiometric mixture of benzene and air, the conversion on the 30% V_2O_5 catalyst at 330 hr^{-1} space velocity dropped from 4% to 1% over 8 hours at 250°C and from 70% to 45% at 450°C for same space velocity and time period. The same catalyst with 0.5% Pd had much higher activity and, though it deactivated at 250°C (68%

to 35% decrease in conversion over 8 hours), the activity actually increased for the same catalyst at 400°C (increasing from 68% to 98% over 8 hours). These observations are explained by the modifying effect of palladium on the oxidation state of the vanadium atoms. The resistance to deactivation is associated with the ability of the palladium to prevent complete reduction of V^{+5} to V^{+3}. The increase in activity of the 30% V_2O_5 plus 0.5% Pd on alumina catalyst at 400°C was accompanied by a moderate reduction of V^{+5} to V^{+4} giving an approximately equal ratio of the two ions. It is suggested that this is also promoted by the presence of palladium.

Cobalt Oxide

Cobalt oxide has been investigated for several oxidation processes, including oxidation of ammonia (for nitric acid production) and automotive exhaust catalysts. In both cases, however, noble metal-based catalysts are used in industrial practice. In the case of automotive exhaust oxidation, cobalt oxides are more resistant to sintering than noble metals but are less active and are subject to SO_2 and SO_3 poisoning (Satterfield, 1980).

One of the more extensive studies of cobalt oxides for oxidation of contaminants in air is that of Pope et al. (1976). They examined several different forms, including Co_3O_4 powder, sintered/unsintered pellets, Co_3O_4 on alumina, and oxide layers on pure cobalt metal (consisting of roughly equal amounts of CoO and Co_3O_4. Screening tests using CO oxidation in an air stream which also contained 3 ppm dimethyl sulfide showed that Co_3O_4 powders, unsintered pellets, alumina-supported Co_3O_4, and oxidized cobalt metal lacked either mechanical strength or sulfur resistance to warrant further attention. All subsequent work was done using unsupported sintered Co_3O_4 pellets. The authors state that the resistance to deactivation by sulfur depends on the "quantity of Co_3O_4 present . . . because the Co_3O_4 surface is renewed as sulfur becomes incorporated by diffusion to the interior" of the particle. This is an interesting mechanism for sulfur tolerance because the catalyst maintained its activity and simultaneously prevented most of the oxidized sulfur in the inlet gas from being emitted in the exit gas. Co_3O_4 pellets used to oxidize a gas containing 4 and 10 ppm dimethyl sulfide retained from 1 to 5 wt% sulfur in the catalyst. Further, when air containing 4 ppm dimethyl sulfide was passed over a fresh catalyst at 215-270°C and 30,000 h^{-1} space velocity, no oxidized sulfur or dimethyl sulfide was observed in the exit gas. When the dimethyl sulfide concentration was increased to 40 ppm and the temperature raised to 433°C, oxidized sulfur did appear in the exit gas. Conversion of dimethyl sulfide initially increased to 15% then decreased to 7% between 75 to 150 hours on stream. These results are thus consistent with the incorporation of sulfur into the catalyst, but also show limits to this process, particularly at high temperatures. Unfortunately, no XRD analysis, which would have perhaps shown the form of the incorporated sulfur, was reported.

Sare and Lavanish (1977a) also discuss the use of cobalt oxide catalysts for oxidation of C_2 - C_4 halogenated hydrocarbons. This study focuses particularly on low temperature oxidation. The activity of cobalt oxide for oxidation of C_2 - C_4 halogenated hydrocarbons is said to drop rapidly at temperatures in the range of 20-50°C, which is not unexpected. The authors also state that though cobalt oxide is somewhat resistant to inhibition by water vapor, such inhibition does occur and is more pronounced at lower temperatures, again as expected. The inhibition by water

is reversible, however. Experimental results are presented for the oxidation of vinyl chloride and vinylidene chloride at 104°C over a catalyst containing 83.3% CoO, though XRD also showed a crystalline cobalt (III) oxide. At 53% relative humidity in the inlet gas and an inlet gas concentration of 46 ppm vinyl chloride and 2.5 ppm vinylidene chloride, initial oxidation was complete but after roughly 3 hours operation, vinyl chloride was detected in the outlet gas (vinylidene chloride was not detected). The activity was restored by decreasing the relative humidity of the inlet gas to 1% (the inlet gas still contained vinyl chloride and vinylidene chloride). Further experiments with a mixture of 10 ppm vinyl chloride, 10.5 ppm vinylidene chloride, 28 ppm methyl chloroform (i.e., 1,1,1- trichloroethane), 20.5 ppm 1,1,2-trichloroethylene and 9 ppm perchloroethylene using a dry air stream (<1% relative humidity) showed that conversion of trichloroethylene, and particularly perchloroethylene, decreased rapidly with time. Conversion of vinyl and vinylidene chloride and methyl chloroform was essentially complete. No further analysis of the catalyst is given, however, nor is any attempt to regenerate the catalyst reported. Finally, the authors report the synthesis of a slightly different cobalt oxide catalyst that is shown to consist of 94.8% cobalt (II, III) oxide (by X-ray spectroscopy). XRD showed crystalline Co_3O_4. This catalyst showed somewhat improved resistance to inhibition by water vapor, even at 60% relative humidity.

Heyes et al. (1982a) also examined Co_3O_4 as a catalyst for oxidation of n-butanal and methyl mercaptan. Using a catalyst prepared by the decomposition of a carbonate precursor (described by Pope et al., 1977), tests showed that at 400°C and 100 ppm of both n-butanal and methyl mercaptan, conversion of methyl mercaptan remained constant at near 100% over 100 hours, but n- butanal conversion dropped to 25% after 50 hours. Simultaneously, the SO_2 content of the exit gas increased and the CO_2 content decreased. Because the reaction of SO_2 with Co_3O_4 is known to produce sulfate in the range 200-500°C (DeBerry and Sladek, 1971) and since SO_2 has been observed to decrease CO oxidation even at 500°C (Farrauto and Wedding, 1973, p. 254) by a sulfate formation mechanism, it is likely that the results of Heyes et al. (1982a) are due to sulfate formation. It is interesting that even water leaching could not restore the CO oxidation activity of the sulfated Co_3O_4 in the study of Farrauto and Wedding (1973) and that no deactivation was observed in the previously discussed study by Pope et al. (1976) in the oxidation of dimethyl sulfide over a limited time frame. This suggests either different means by which sulfur is incorporated into the cobalt catalyst or different types of sites for CO oxidation versus dimethyl sulfide oxidation.

Copper Oxide

Copper oxide is not widely used as an oxidation catalyst for emissions control, though it is a component of several better known mixed oxide oxidation catalysts, like copper chromite and hopcalite (both discussed later). Industrially, it is used for the partial oxidation of propylene to produce acrolein, a precursor of acrylic acid.

Several reports of the use of CuO for control of trace contaminants in air have compared its performance, including deactivation, with other catalysts. Heyes et al. (1982a) examined CuO for the oxidation of n-butanal and methyl mercaptan. Of interest is that its activity at 400°C for

107

n-butanal oxidation (100 ppm in air), even in the presence of 100 ppm methyl mercaptan, was higher than for MnO_2, Co_3O_4, or V_2O_5 and was approximately equal to a platinum-Thermacomb catalyst. However, over the 150 hour test, steadily decreasing amounts of CO_2 and increasing amounts of CO and SO_2 were detected in the outlet gas, suggesting sulfation of the catalyst that may have affected selectivity for CO_2 formation. XRD of the catalyst after the test showed CuO with hydrated and anhydrous copper sulfate as well as copper formates. Thus, the ca alyst must eventually deactivate to the point where n-butanal and methyl mercaptan conversion would be incomplete. Based on the gradual sulfating of copper oxide when used to control sulfur-containing compounds, Heyes et al. (1985) then examined the use of copper sulfate as a starting catalyst for oxidation of the same compounds. Copper sulfate produced dimethyl disulfide between 100°C and 200°C. SO_2 became the main sulfur product. After 100 hours at 400°C, little deactivation was observed and the "removal" of methyl mercaptan and n-butanal (which simply compared inlet and outlet levels of these compounds, not necessarily whether they are completely oxidized or not) was complete.

Yao (1984) looked at CuO as an automotive exhaust catalyst for ethanol powered vehicles. They evaluated CuO catalysts (on $-Al_2O_3$, ZrO_2, and $CeO_2/-Al_2O_3$) using a simulated exhaust gas of 1% O_2 and 0.14% ethanol (in helium). $CuO/-Al_2O_3$ had the highest activity, as measured by the lowest temperature required to produce no detectable ethanol in the exit gas. CuO loadings of up to 11.5 wt% were then evaluated. Exposure to temperatures of 600-1000°C for 16 hours, presumably in air, resulted in progressively lower activity for catalytic oxidation, with particularly significant deactivation from 800 to 1000°C. The specific surface area of the catalyst decreased from 120 m^2/g after exposure at 600°C, to 80 m^2/g at 800°C, to 12 m^2/g at 1000°C. Attempts to stabilize the $-Al_2O_3$ support (which is known to be transformed to low surface area $\alpha-Al_2O_3$ at these temperatures) with CeO_2 only marginally improved the thermal stability. The addition of 2% water vapor inhibited the oxidation of ethanol for all three copper catalysts. This is attributed to the adsorption of H_2O on the catalyst surface which competes with the adsorption of ethanol.

Farrauto and Wedding (1973) studied the deactivation of CuO catalysts (by SO_2) as applied to automotive exhaust catalysts. They used an unsupported, essentially non-porous, CuO catalyst (0.1 m^2/g) prepared by decomposition of copper nitrate. Exposure to 100 ppm SO_2 at 500°C rapidly decreased the CO oxidation activity. Attempts to restore the activity by water leaching resulted in catalyst with no more than 20-30% of its original activity. XRD showed that $CuSO_4$ had been found.

Copper catalysts are also subject to deactivation by chlorine. Ostrovoskii et al. (1987) examined the long-term poisoning of a CuO-based catalyst used for treatment of autoclave synthesis waste gases (contents not disclosed), but the deactivation was shown to be irreversible and due to interaction of Cu with S- and Cl- compounds. No discussion of regeneration was given, but "the thermodynamic analysis of the poisoning process was in agreement with physiochemical investigations". If this is so, it might be worth investigating the "thermodynamic analysis" in more detail.

Earlier work has reported extensively on the characteristics of the Deacon Process (HCl + O_2, Cl_2 + H_2O), where copper based catalysts are extensively deactivated by volatilization of $CuCl_2$ at the temperatures employed, normally around 600°C. (Satterfield, 1980, p. 206). There is some indication that these can be stabilized by alkali such as Ba but few specific studies are available.

Chromium Oxide

Chromium oxide has been studied, in various forms, as a catalyst for oxidation as well as for other processes such as dehydrogenation (Satterfield, 1980). Though it is usually prepared by impregnation of a support such as $-Al_2O_3$, the use of crystalline $\alpha-Cr_2O_3$ as an unsupported catalyst has also been reported (Yao, 1973). It can also be alloyed with other metals to form active oxidation catalysts such as copper chromite (discussed later).

Manning (1984) examined a 12.5 wt% Cr_2O_3/Al_2O_3 catalyst for the oxidation of various chlorinated compounds. Tests with perchloroethylene, C_2Cl_4, showed a decrease in activity with time in a dry air stream. This deactivation was faster with a higher concentration of perchloroethylene. Though no inhibition due to water vapor was found to perchloroethylene oxidation, water vapor did inhibit the oxidation of di-and trichloroethylene on this catalyst. Longer tests (over a 24 hour period) in dry air showed significant decrease in perchloroethylene conversion over time, dropping from near 100% to near zero first over 8 hours at a concentration of 1.58 mole% and then over 24 hours at a concentration of 0.83 mole%. During the runs made at these conditions, a red deposit at the reactor exit and analysis of the chromia catalyst together suggested loss of chromia from the catalyst. Manning suggests that in the absence of water, the Cl_2 produced in the oxidation of C_2Cl_4 reacted with the Cr_2O_3 catalyst to produce red chromium oxychloride, CrO_2Cl_2. The addition of water to the feed stream significantly reduces deactivation rate, probably due to the Deacon reaction, $2HCl + O_2 \rightleftharpoons H_2O + Cl_2$, which removes Cl_2 from the product gas, reducing the formation of CrO_2Cl_2, which would presumably prevent chromia from being removed from the catalyst surface.

Young (1982) investigated the oxidation of methylene chloride over a commercial 12.5 wt% chromia/alumina catalyst. Young reports a significant increase in CO content, and decrease in CO_2 content, of the exit gas over time, though this is not related to any observable change in catalyst composition, e.g. halogen or carbon disposition on the catalyst. It is postulated, however, that chloride or perchlorate formation may occur on the catalyst. It is also observed that the addition of water inhibits the formation of Cl_2 and heavier (than methylene chloride) chlorinated hydrocarbons, which were observed in the absence of added water vapor in the inlet gas. However, the addition of water, by itself, does not affect selectivity to oxides of carbon, CO + CO_2. Michalowicz (1982) examined the oxidation of chlorinated ethylene on 12.5 wt% $Cr_2O_3/alumina$ and $Cr_2O_3/silica$ (chromia content not given), among other catalysts. On the chromia/alumina catalyst, the formation of chlorinated hydrocarbon polymers was observed both downstream of the catalyst and presumably on the catalyst as well in the oxidation of trichloroethylene. This is said to be formed by the reaction of Cl_2 formed in the oxidation reaction with "chlorinated trichloroethylene". The addition of water to the inlet gas increased

109

both the conversion and CO_2 yield and produced less polymers. Further increase in water content of the inlet gas (resulting in a hydrogen/chlorine atomic ratio of 2.94) caused essentially complete conversion and no polymer formation. Further, no deactivation was observed after 24 hours. Using the Cr_2O_3/Al_2O_3 catalyst to oxidize perchloroethylene resulted in a decrease in conversion from 98% to 53% over a 17 hours at 766°C. This was correlated with a loss of chromia from the catalyst, with the chromia content dropping from 12.5% to about 7.5% over this run. The addition of water vapor slowed the deactivation but did not eliminate it. EDAX analysis showed that the absence of water resulted in chloride deposition on the catalyst surface. The deactivated catalyst could be partially regenerated by hot air. Other tests lead the author to suggest molecular chlorine as the species responsible for the deactivation. There are thus two forms of deactivation observed on this catalyst. First, there is reversible adsorption of Cl_2 which is adsorbed selectively on sites active for oxidation. This is more prevalent at lower temperatures. This adsorbed chlorine is apparently reacted to HCl (via the Deacon reaction) in the presence of water vapor, resulting in less deactivation. Second, there is the loss of chromium metal by volatilization of chromium chloride or chromium oxychloride, both of which have significant vapor pressures at 550°C.

Hunter et al. (1982) discuss the commercial application of a catalyst described only as "15 to about 25% by weight chromic oxide, the balance being alumina or other carrier or support". The catalyst is designed for use in a fluidized bed where the normal attrition of the catalyst is designed to constantly expose fresh catalyst, with the deactivated catalyst removed as particles from the bed. In one example given in this patent, Hunter et al. report no catalyst loss over a six week period in oxidizing a gas containing ethanol, acetic acid, and other organics associated with vinegar production.

Finally, Yao (1973) looked at four α-Cr_2O_3 crystals (surface areas of 0.15 - 1.96 m^2/g) for oxidation of C_2 - C_3 olefinic and paraffins and CO. For C_2 - C_3 hydrocarbon oxidation, the water inhibited the reaction. An initial increase or decrease in the oxidation rate before a steady value was reached, called "self deactivation", was observed. Over one of the Cr_2O_3 catalysts, some reaction conditions led to deactivation in olefin oxidation and a shortfall in the carbon material balance. This suggested some deposition on the catalyst. Heating the catalyst at 500-600°C in a mildly oxidizing gas restored the activity and generated a small amount of CO_2 (0.01 - 0.02 mL CO_2/m^2). This suggests that the unconverted carbon is retained on the catalyst as an oxidizeable low volatile compound and that it probably poisons the most active sites selectively. This deactivation was not observed for paraffin oxidation. The addition of SO_2 to a mixture of O_2, C_3H_6, and helium decreased the reaction rate. At monolayer coverage, the rate was 20% of the original rate, suggesting that SO_2 does not selectively adsorb at active sites. Heating to 800°C in a mild oxidizing gas restored the activity to 70% of the original. Ammonia reversibly suppressed C_3H_6 oxidation while it itself was converted to N_2O at a slow rate.

Manganese Oxide

Manganese oxide, like chromium oxide, is generally most often used with other metals to form an active oxidation catalyst, e.g., the well known hopcalite consisting of manganese and copper oxides. However, it has also been studied as a catalyst in its own right.

Reported work on deactivation of MnO_2 as an oxidation catalyst consists principally of that reported by Heyes et al. (1982a, 1985) out of the Warren Spring Laboratory in England. In the first study (Heyes et al., 1982a) oxidation of 100 ppm methyl mercaptan in air was essentially complete at temperatures above 120°C. After 70 hours, the temperature required for complete removal of this sulfur-containing compound was unchanged. However, all the sulfur and carbon in the mercaptan was not accounted for as SO_2 and CO_2 at all temperatures tested, suggesting eventual deactivation. Extended tests at 400°C over 120 hours for the oxidation of 100 ppm of both methyl mercaptan and n-butanal also showed a shortfall in the carbon balance (as CO_2 + CO) after 50 hours. Analysis of the catalyst by XRD indicated the formation of $MnSO_4$ and possibly $MnS_{0.6}O_3$. However, the sulfated catalyst remained active for mercaptan oxidation and showed only a slight decrease in conversion (to 85% from near 100%) of n-butanal.

The second study (Heyes et al., 1985) extended their earlier work by using manganese sulfate as the starting material for oxidation, arguing that it might represent a "stabilized" form of MnO_2 for oxidation of sulfur-containing compounds. After heating the $Mn(SO_4)_2$ to 250-260°C to remove the water of hydration, the catalyst was used to oxidize 100 ppm methyl mercaptan at 22500 hr^{-1} space velocity at various temperatures. At 240°C, mercaptan conversion reached a minimum of 35%, and the activity could be restored by passing air at 277°C for 1.5 hours over the catalyst. Further tests starting with MnO_2 at 300°C for mercaptan oxidation were made to compare the performance of manganese sulfate and a "sulfated" MnO_2, which was made by oxidizing methyl mercaptan over a MnO_2 catalyst. Differences were observed that were explained by the presence of two types of sites on the $Mn(SO_4)_2$ that are not present on the sulfated MnO_2, one of which is active at lower temperatures and the other of which is active at higher temperatures. For simultaneous n-butanal and methyl mercaptan oxidation at 400°C on the $Mn(SO_4)$ catalyst, n-butanal removal fell from 90% to 45% over 100 hours. Mercaptan removal remained near 100%, but sulfur in the exit gas (as SO_2 + dimethyl disulfide) was not sufficient to close the material balance.

Mixed Metal Oxides

Mixed metal oxides have been widely used, and studied, for catalytic oxidation. These catalysts are usually supported on a carrier such as $-Al_2O_3$, but may also be used without a support. As a general rule, they are more active and poison tolerant over a range of inlet gas compositions. The activity and deactivation resistance of a mixed oxide catalyst cannot be directly inferred from the behavior of the single metal oxide components.

111

Hopcalite (MnO$_2$/CuO)

Hopcalite is a compound consisting of roughly 78% MnO$_2$ and 13% CuO, the balance being primarily water of hydration. The ratio of MnO$_2$ to CuO may vary slightly with different samples of the catalyst. Hopcalite may be used as unsupported material or may be impregnated on a support such as alumina.

Military uses of hopcalite as an air purification catalyst have been reported by several studies at the Naval Research Lab (Washington, DC). Christian and Johnson (1965) examined the catalytic oxidation of compounds found in a submarine environment over hopcalite. These compounds included light hydrocarbons as well as hydrocarbons containing oxygen, nitrogen, and halogens. During an 8-hour run at 315°C, the conversion of Freon 114B2 (C BrF$_2$ - C BrF$_2$) fell from 30% to 5%. Most of the fluoride and some of the bromide was retained on the catalyst. At this same temperature, conversion of 1,1,1-trichloroethane fell from 50% to 32% over 6.5 hours, with results again showing most of the halogen retained on the catalyst. This deactivation was also apparently accompanied by a change in selectivity with time. Specifically, the formation of vinylidene chloride and trichloroethylene was observed.

Later work at the Naval Research Lab also investigated the catalytic oxidation of several compounds over hopcalite (Musick et al., 1972). The activity for CO oxidation dropped drastically when thiophene was added to the inlet gas, but the activity could be partially restored by removing thiophene from the inlet gas. Activity could be further restored by exposure to cool, humid, pure air.

A patent describing a manganese oxide/copper oxide catalyst with a "typical" ratio of 6/1 to 8/1 has been reported (Sare and Lavanish, 1977b). Though the patent claims are very broad and are not limited specifically to hopcalite, hopcalite (as 81% MnO$_2$, 10% CuO) is used in examples of experimental data. Oxidation of 50 ppm vinyl chloride in dry air (dewpoint less than 25°C) at temperatures from 23 to 340°C over a period of roughly 8 hours showed no deactivation. However, when left overnight at 81°C with 43 ppm vinyl chloride in the inlet gas, the conversion dropped from 100% to 37%. XRD indicated structural changes had occurred, specifically that some chloride had been formed on the catalyst. The authors suggest that HCl and water vapor, produced by the oxidation of vinyl chloride, are adsorbed on the catalyst. Passing dry air at 100-200°C over the deactivated catalyst is said to regenerate it. Also, oxidation at lower temperatures, near ambient, seem to promote rapid deactivation, with higher reaction temperatures (in the range of 100-200°C) apparently assisting in the removal of HCl, CO$_3$, and water from the surface.

Copper Chromite

Copper chromite, in various forms, has been investigated for use as an automotive exhaust catalyst and for other oxidation processes. Its use for automotive purposes was limited due to its tendency to sinter at high temperatures (Satterfield, 1980) and to form sulfates (Hegedus and

McCabe, 1984). Nevertheless, it can be used in certain applications of interest to the Air Force where temperatures are less demanding.

Farrauto and Wedding (1973) studied copper chromite catalysts. One was a low surface area (6 m²/g) acid leached $CuCr_2O_4$ (designated L - $CuCr_2O_4$) catalyst prepared from aqueous nitrate precursors and subsequent HCl leaching. The second, calcined at 800°C, was a commercial $Cu_2Cr_2O_4$ catalyst (Harshaw 1800P) containing excess CuO (51% CuO, 47% Cr_2O_3, compared to 34 wt% CuO and 66 wt% Cr_2O_3 for stoichiometric $CuCr_2O_4$). The L- $CuCr_2O_4$ was expected to be more thermally stable, with no chemical or physical changes observed up to 800°C. However, exposure of L - $CuCr_2O_4$ to SO_2 at various temperatures showed a strong deactivation as measured by CO oxidation activity and, separately, by hexane oxidation activity. The catalyst was severely deactivated by exposure to 800 ppm SO_2 at room temperature, 400°C, and 700°C, but could be regenerated by exposure to air at 800°C for 24 hours. [Similar poisoning by sulfur oxides was observed by Desai et al., (1987) on a 10% $CuCr_2O_4$/alumina catalyst at 575°C, losing 50% of its activity for the oxidation of vapors generated from spent ion exchange resins in 1 hour]. Thermal gravimetric analysis (TGA) of the poisoned samples from these tests showed lower overall loss of SO_2 from the sample exposed at 800°C, suggesting stronger bonding of SO_2 with the surface at 400 and 700°C, as might be expected. At 800°C, there was no difference in CO oxidation activity between L-$CuCr_2O_4$ catalysts treated at 800°C with 800 ppm SO_2 and those treated at 800°C with no SO_2. Temperature programmed reaction (TPR) tests on fresh L-$CuCr_2O_4$ from 100 to 800°C in air containing 1000 ppm SO_2 showed SO_2 to be adsorbed up to about 575°C, then desorbed at higher temperatures, with about half the SO_2 remaining on the catalyst at 800°C. Infrared analysis showed no sulfate formation for $CuCr_2O_4$ exposed to up to 10^4 ppm SO_2 at 400°C or 500°C, though bands assigned to adsorbed SO_2/SO_3 were found. Exposure to either 10^3 or 10^4 ppm SO_2 at 500°C caused the catalyst to lose essentially all its activity, as measured by CO oxidation below 200°C. However, water washing restored its original activity. In parallel tests, the Harshaw 1800P showed rapid decrease in CO oxidation activity at 500°C when 100 ppm SO_2 was present in the gas stream. Water washing restored only 20- 30% of the original activity. XRD showed $CuSO_4$, as expected given the stoichiometric excess of CuO in the original sample. From all the evidence, Farrauto and Wedding conclude that the Harshaw 1800P copper chromite is resistant to sulfur formation below 400°C. The L-$CuCr_2O_4$ is poisoned by strong chemisorption of SO_2 though there is no evidence of sulfate up to 700°C. Further, no poisoning occurs on L-$CuCr_2O_4$ in an atmosphere of 800 ppm SO_2 up to 800°C. Two types of oxidation sites, one apparently active for CO oxidation ("carbonyl") and the other for hydrocarbon (hexane herein) oxidation ("carbonate"), are identified. SO_2 selectively adsorbs on the carbonyl sites at low temperatures and on the carbonate sites at higher temperatures.

Interaction of copper chromite catalysts with sulfur- containing compounds was also investigated by Heyes et al. (1982b). Using a commercial catalyst (Harshaw Cu-0203T) containing 80% CuO and 20% Cr_2O_3 (apparently not $CuCr_2O_4$), they measured the conversion of methyl mercaptan and n-butanal. For oxidation of 100 ppm methyl mercaptan alone, conversion was complete over the range 100° - 400°C, but all sulfur and carbon were not accounted for, especially at the higher temperatures. This suggests eventual loss of activity and accumulation of sulfur and carbon, in some form, on the catalyst. At 400°C, a mixture of 100 ppm of both

113

n-butanal and methyl mercaptan was initially completely removed from the inlet gas, but a material balance on carbon (as $CO + CO_2$) decreased from 90% to 75% over 100 hours, with an increasing proportion of CO. Initially little SO_2 was formed, but as the catalyst apparently became sulfated, sulfur recovery increased to 76% as SO_2 after 75 hours. This is not surprising since similar behavior was observed in the same study with the CuO catalyst which contained considerable excess CuO. Farrauto and Wedding (1973) also observed copper sulfate formation above 400°C for the Harshaw 1800P copper-chromite catalyst containing excess CuO. Tests at 400°C using 100 ppm of both methyl mercaptan and n-butanal were carried out until deactivation began (50 hours). The catalyst was then water washed. The activity was restored and copper sulfate, along with traces of chromium, were found in the water. XRD showed CuO as the major phase with $CuCr_2O_4$ also present. Further tests were done on this leached catalyst at lower temperatures (300°C) at higher reactant concentrations until conversion began to drop. A second water leaching showed copper and traces of chromium, but very little sulfate. This second wash also restored the original activity. Field tests of a copper chromite catalyst on process gas containing H_2S, methyl mercaptan, n-aldehydes, and furfural showed deactivation only to 94% of the original value after 2000 hours on stream.

Two studies by Severino and co-workers (Severino and Laine, 1983; Severino et al., 1986) examined various forms of copper chromite for CO oxidation. In the first study (Severino and Laine, 1983), a number of alumina supported and unsupported catalysts were examined to determine the effect of the various metal components and supports. A test with a commercial unsupported Harshaw Cu-0203 catalyst (Cr/Cu + Cr weight ratio of 0.15) showed deactivation (as measured by CO oxidation activity at 200°C) after CO oxidation at 400°C for 1 hour. Activity could not be completely restored by reduction in CO at 300°C. This is explained by a shift in the oxide-reduced copper equilibrium (at the catalyst surface) being shifted toward the oxide at higher temperatures, which are said to be the active oxidation sites. This oxidation is apparently only partially reversible by CO reduction at 300°C. Similar behavior was observed with other laboratory prepared copper chromites. The introduction of 15% water vapor drastically decreased the CO oxidation activity (at 400°C) for 10 and 20% $CuCr_2O_4/Al_2O_3$ catalysts. Further work from the same labs focused on only alumina supported copper chromite catalysts (Severino et al., 1986). This catalyst showed no deactivation for CO oxidation at 200°C over 6 hours for a series of catalysts containing 2, 5 and 30 wt % Cu + Cr. Based on parallel studies on supported CuO, the authors speculate that the resistance to deactivation is due to the fact that the active copper sites in $CuCr_2O_4$ are more stable. Deactivation appears to be oxidation of the copper sites, as suggested by their earlier work (Severino and Laine, 1983).

Manganese/Cobalt

This catalyst is not widely used industrially but is reported in at least one patent to be useful for oxidation of chlorine-containing hydrocarbons such as vinyl chloride (Sare and Lavanish, 1977b). As with other metal oxides, the inhibition by water vapor is important, with higher humidities requiring higher temperatures to achieve a given conversion. Resistance to this inhibition is greater with higher proportions of manganese than cobalt. The inhibited catalyst can

114

be regenerated by dry air at 150-200°C. Catalyst activity falls off rapidly with time at temperatures near ambient, e.g. 20-50°C.

The authors describe the oxidation of a gas containing 38 ppm vinyl chloride and 3 ppm vinylidene chloride (in air) using an unsupported catalyst containing 78.5 wt % MnO_2 and 11.9 at % CoO (the balance presumably being water of hydration and impurities). At 104°C, the catalyst activity (as measured by the disappearance of the chloride compounds in the inlet gas) decreases rapidly at 50 % relative humidity. The activity can, however, be restored by contacting the catalyst with dry inlet gas, even if it contains the vinyl and vinylidene chlorides. A catalyst of different composition (60.5 % Co_3O_4, 28.9 % MnO_2) was then used to oxidize various mixtures containing 8-10 ppm vinyl chloride, 9-11 ppm vinylidene chloride, 39-41 ppm methyl chloroform (1,1,1-trichloroethane), 19-26 ppm trichloroethylene, 1.5-2 ppm 1,1,2-trichloroethane and 10-14 ppm perchloroethylene. After 5.5 hours at 188°C, no loss of activity (again measured only by the disappearance of the compounds in the inlet gas) was observed except for perchloroethylene. When the temperature was then lowered to 104°C, there was some loss of activity compared to an earlier run at the same temperature, indicating some deactivation.

High temperatures may also deactivate the catalyst. When an alumina support is used, Yao (1974) reports the formation of inactive $CoAl_2O_4$ at temperatures above 850°C.

Cobalt Molybdate

Cobalt molybdate, supported on alumina, is a well known hydrodesulfurization catalyst. This is normally 3-5% CoO and 8- 15% MoO_3 on -alumina. Because of the high activity of this catalyst in its sulfided form, it has been investigated as an oxidation catalyst for sulfur-containing compounds. This resistance to poisoning may be limited to reduced sulfur compounds (e.g., H_2S, mercaptan) in the inlet gas rather than SO_2. For example, Desai, et al. (1987) observed rapid deactivation of an alumina supported cobalt molybdate when exposed to a gas containing oxidized sulfur compounds.

Heyes et al. (1982b) investigated the oxidation of 100 ppm n-butanal and 100 ppm methyl mercaptan over a 5% $CoO-MoO_3/Al_2O_3$ catalyst at 400°C. After 100 hours, removal of the mercaptan was complete, but n-butanal removal dropped from 94% to 89%. Recovery of sulfur (as SO_2) and carbon (as $CO + CO_2$) was incomplete throughout the test, suggesting some retention of sulfur and carbon by the catalyst.

Using an unsupported, hydrated $CoMoO_4$ catalyst, Ross and Sood (1977) also investigated the oxidation of methyl mercaptan. No loss of activity was observed over 100 hours in oxidizing 1000 ppm methyl mercaptan in dry air at 400°C. XRD showed no change in the catalyst, though its surface area decreased from 14.5 to 6 m^2/g. Using a concentration of 400 ppm methyl mercaptan and 4% oxygen, reversible inhibition by water was observed at water contents of 0.5 and 1% at temperatures below 360°C. Above 360°C, water vapor had little effect on activity. Water vapor also suppressed the formation of dimethyl disulfide in the exit gas, indicating some selectivity of the water vapor in its interaction with the surface. Further evidence presented by

the authors suggests that water vapor selectively adsorbs at the same anion vacancies as those active for adsorption of the sulfur atom in the reactant, methyl mercaptan. This selective adsorption, however, is not likely above 340°C, the dehydration temperature for this catalyst.

Other Metal Oxides

In addition to the single and bimetallic metal oxides discussed above, several references discuss more complex oxides of interest. For example, Takakuwa et al.(1982) claim the development of a poison-tolerant catalyst for the oxidation of styrene, C_6H_5-CH=CH$_2$. The catalyst is a complex oxide mixture on alumina (CrO$_3$ - CuO - NiO - Al$_2$O$_3$), and poisoning was investigated after impregnation with solutions of Pb, Hg, Cd or As, with good activity maintenance after exposure to these materials.

Three additional catalyst formulations that may be worth future investigations are reported by Terlyanskaya and Sorokina (1982) for dimethylformamide removal and Dimitrov et al. (1983) for oxidation of o-xylene and m-cresol. The former is a mixture of Al$_2$O$_3$ - Fe$_2$O$_3$ - RuO$_2$ - BaO - CuO, with the predominant components Al$_2$O$_3$ (~65%) and Fe$_2$O$_3$ (~15%). The latter compared a Co$_3$O$_4$CuO with a typical supported CuO in the range of 500-550°C. There was an apparent high initial activity for the Co-Cu formulation, however only CuO - Al$_2$O$_3$ was stable in an extended life test.

Two additional references, not available in translation, may also have pertinence in study of deactivation of VOC catalysts (Elagina and Sheveleva, 1981; Sazanov and Pavlova, 1982).

116

REFERENCES

Ahmed, K., D. Chadwick, L. S. Kershenbaum, Stud. Surf. Sci. Catal., Elsevier, 34, 1987, 513-521.

Bond, G.C., Sadeghi, N., Catalysed Destruction of Chlorinated Hydrocarbons," J. Appl. Chem. Biotechnol. 1975, 25, 241-248.

Bourne, K. H., P. D. Holmes, R. C. Pitkethly, 3rd Int. Cong. Catal., North Holland, 1954, 1400-1415.

Butt, J. B., "Advances in Chemistry," V. 109, American Chemical Society, 1972, 259-496.

Butt, J. B. and E. E. Petersen, Activation, Deactivation, and Poisoning of Catalysts, Academic Press, New York, 1988.

Christian, J. G. and J. E. Johnson, Int. J. Air Water Poll., 9, 1965, 1-10.

Cullis, C.F., Keene, D.E., Trimm, D.L., J. Catal. 1970, 19, 378- 385.

Cullis, C.F., Willatt, B.M., J. Catal. 1983, 83, 267-285.

Dalton, A. I. and S. Sircar, U.S.P. 4,346,019, August 24, 1982.

DeBerry, P. W., K. Sladek, Canadian J. Chem. Eng., 49, 1971, 791.

Desai, F. N., H. L. Greene, P. Subbanna, Ind. Eng. Chem. Res., 26, 1987, 1965-1969.

Duprez, D., Mendez, M., Stud. Surf. Sci. Catal., 34, Elsevier, 523-534, 1987.

Elagina, E.D., Sheveleva, T.V., "Catalytic Detoxication of Gaseous Emissions Containing Toxic Organic Compounds," from Ref. Zh. Khim. 1981, Abstract 151652 (in Russian).

Farrauto, R. J., B. Wedding, J. Catalysis, 33, 1973, 249-255.

Guo, I., Yu, T.T., Wanke, S.E., Catalysis, 1987, Elsevier, New York, 1988, 21-32.

Hegedus, L. L. and R. W. McCabe, Catalyst Poisoning, Marcel Dekker, New York, 1984.

Heyes, C. J., Jr., G. Irwin, H. A. Johnson, R. L. Moss (1982a), J. Chem. Tech. Biotechnol., 32, 1982, 1034-1041.

Heyes, C. J., J. G. Irwin, R. L. Moss, (1982b), J. Chem. Tech. Biotechnol, 35A, 1985, 89-96.

Hughes, R., Deactivation of Catalysts, Academic Press, New York, 1984.

Hunter, W. K., L. C. Hardison, E. J. Dowd, U.S.P. 4,330,513, May 18, 1982.

Hucknall, D. T., B. M. Willatt, R. J. Hockham, Catalyst Deactivation, Elsevier, 1980, 213-232.

Irwin, J. G., T. A. Dorlina, R. L. Moss, Atmos. Env., 13, 1979, 1569-1579.

Kawahata, M., Lazzaro, R., "Poisoning of Catalytic Methane Sensors," prepared for Bureau of Mines, Washington, DC, 1981.

Lavanish, J. M. and E. J. Sare, U.S.P. 4,039,623, August 2, 1977.

Lieske, H., G. Leitz, H. Spindler, J. Volter, J. Catalysis, 81, 8, 1983.

Leitz, G., H. Lieske, H. Spindler, W. Hanke, J. Volter, J. Catalysis, 81, 17, 1983.

Lindberg, R.C., Reedy, J.D., Yang, K., U.S.P. 4,059,683, November 22, 1977.

Manning, P. Hazard. Waste, 1984, 1 (1), 41-65.

Martin, N.A., Final report for EPA Contract 68-02-3133, EPA- 600/S2-81-017, 1981; EPA, Washington, DC.

Megiris, C.E., Butt, J.B., Proc. 9th Int. Symp. on Catalyst Deactivation, Basel, Switzerland, 1988.

Mendyka, B., and Rutkowski, J.D., Environ. Prot. Eng., 10, 5, 1984.

Michalowicz, R., "The Oxidation of Chlorinated Ethylenes Using Selected Catalysts," M. S. Thesis, MIT, Cambridge, MA, September 1982.

Moon, S. H., S. W. Lee, B. P. Sung, Hwahak Konghak, R5(5), 1987, 468-476 (in Korean).

Musick, J.K., Thomas, F.S., Johnson, E.J., Ind. Eng. Chem. Process Des. Dev, 1972, 11 (3), 350-354.

Ostrovoskii, Yu.V., Ryabtsev, A.D., Zabortsev, G.M., Shpak, A.A., Popovskii, V.V. and Sazonov, V.A., Ah. Prikl. Khim., 60, 1470, 1987 (in Russian).

Palazzolo, M. A., R. M. Parks, K. K. Fidler, "Control of Industrial Emissions by Catalytic Incineration," EPA-600/2- 84-1186, July 1984.

Patterson, W.R., Kemball, C.J., Catal. 1963, 2, 465-478.

Pope, D., Walker, D.S., Moss, R.L., Atm. Environment, 10, 951, 1976.

Pope, D., Walker, R. L., Moss, J. Catalysis, 47, 1977, 33.

Pope, D., Walker, D.S., Moss,R.L., Atmos. Environ. 1978, 12, 1921-1927.

Rossin, J. A., Ind. Eng. Chem. Res., November 1989 (in press).

Sadamori, H., A. Chikazawa, S. Okamura, R. Noda, 1981 International Gas Research Conference, 1467-1486.

Sare, E. J. and J. M. Lavanish, (1977a), U.S.P. 4,065,543, December 17, 1977.

Sare, E. J. and J. M. Lavanish (1977b), U.S.P. 4,045,538, August 30, 1977.

Satterfield, C. N., *Heterogeneous Catalysis in Practice*, McGraw Hill, New York, 1980.

Sazonov, V.A., Pavola, S., "Study of the Action of Catalytic Poisons on Catalysts of Complete Oxidation," from Ref. Zh. Khim. 1982, Abstract L262 (in Russian).

Severino, F., Brito, J., Carias, O., Laine, J., J. Catal. 1986, 102, 172-179.

Severino, F., Laine, J. Ind. Eng. Chem. Prod. Res. Dev. 1983, 22, 396-401.

Shelef, M., K. Otto, N. C. Otto, Advances in Catalysis, 27, Academic Press, New York, 1978, 311-365.

Spivey, J.J., "Complete Catalytic Oxidation of Volatile Organics," I&EC Research, 1987, 26, 2180.

Szepsey, L., Welther, K., Sebestyen, Zx. Hung. J. Ind. Chem. 1978, 6, 11-20.

Takakuwa, L, Iwasaki, T., Itaneda, H., Yokohama, S., and Seisho, M., Kogai, 17, 171, 1982.

Tejima, N., Kato, Y., Konishi, K., Matsuda, T., Ebina, T., Jap. Kokai Tokkyo Koho JP 63, 240, 951, October 6, 1988.

Terlyanskaya, A.T., Sorokina, N.P., USSR SU 954,098, 30 August, 1982.

Vassileva, M., A. Andreev, S. Dancheva, N. Kotsev, Appl. Catalysis, 49, 1989, 125-141.

Volter, J., Lietz, G., Spindler, H., Lieske, H., J. Catal. 1987, 104, 375-380.

Wainright, M.S. and Foster, N.R., Catal. Rev.-Sci. Eng., 19, 1979, 211.

Wanke, S. E., P. C. Flynn, Catal. Rev. Sci. Eng., 12, 1975, 93.

Yang, K. and J. D. Reedy, U.S.P. 4,059,676, November 22, 1977.

Yao, Y.F.Y., Kummer, J.T., J. Catal. 1973, 28, 124-138.

Yao, Y.F.Y., Ind. Eng. Chem. Process Des. Dev. 1984, 23, 60-67.

Young, P. D., "Kinetic Study of the Catalytic Oxidation of Dichloroethane," M. S. Thesis, MIT, Cambridge, MA, June 1982.

NOTICE

PLEASE DO NOT REQUEST COPIES OF THIS REPORT FROM
HQ AFESC/RD (ENGINEERING AND SERVICES LABORATORY).
ADDITIONAL COPIES MAY BE PURCHASED FROM:

> NATIONAL TECHNICAL INFORMATION SERVICE
> 5285 PORT ROYAL ROAD
> SPRINGFIELD, VIRGINIA 22161

FEDERAL GOVERNMENT AGENCIES AND THEIR CONTRACTORS
REGISTERED WITH DEFENSE TECHNICAL INFORMATION CENTER
SHOULD DIRECT REQUESTS FOR COPIES OF THIS REPORT TO:

> DEFENSE TECHNICAL INFORMATION CENTER
> CAMERON STATION
> ALEXANDRIA, VIRGINIA 22314